THERMAL STABILITY AND DEGRADATION OF SOME POLYACRYLATE SALTS

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SUMMARY

The work carried out in this study has involved the preparation, characterisation and subsequent thermal degradation of homopolymers and copolymers with structures based on metal salts of acrylic acid.

Four transition metal salt homopolymers of poly(acrylic acid) were prepared and characterised. The polymers were prepared by polymerisation of metal acrylate monomer and neutralisation of poly(acrylic acid) by the appropriate metal salt. The metals used were cobalt, nickel, copper and zinc. Three copolymers of acrylic acid with styrene and their zinc salts were also prepared. These copolymers contained 1.7%, 5.8% and 11.8% acrylic acid units.

The second section of the work involved the thermal degradation of these polymers and copolymers. The thermal degradation experiments were carried out either by ramped programmed or isothermal heating in oxygen free environments.

The techniques used to study the thermal degradation of the polymers were thermogravimetry (TG), differential thermal analysis (DTA) direct scanning calorimetry (DSC) and thermal volatilistaion analysis (TVA), with fractionation of the products of degradation by sub-ambient TVA.

Mechanisms of polymer degradation are discussed with respect to the degradation products obtained during TVA. The degradation products were identified by mass spectroscopy, gas chromatography-mass spectroscopy and fourier transform infra-red spectroscopy.

The thermal degradation of transition metal salts of poly(acrylic acid) occurred by a free radical decomposition process. The thermal stability of the polyacrylates was affected by the particular metal involved. The metal polyacrylates followed the stability sequence Zn=Co>Ni>Cu. The polymers made by neutralisation of poly(acrylic acid) and those made by polymerisation of metal acrylate monomer exhibited similar thermal stability and degradation characteristics.

The thermal degradation of the three copolymers of acrylic acid with styrene and the zinc salts of these copolymers occurred by a free radical mechanism. The thermal stability of the copolymers decreased with increasing acrylic acid content. The zinc salt copolymers showed a slight increase in thermal stability compared to the acid copolymer In isothermal heating experiments the rate of degradation of the acid copolymers was decreased by converting them to their zinc salts.

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CHAPTER ONE

INTRODUCTION

1.1 BRIEF HISTORY OF POLYMER SCIENCE

The abundance of macromolecules, both natural and synthetic, makes them one of the most significant and interesting areas of science. Naturally occurring biological polymers such as wool, cotton, resins, gums and amber have been used for thousands of years, but the understanding and development of synthetic polymer science is a much more recent phenomenon.

The polymer scientists of the nineteenth and early twentieth century based their work on empirical observations, without the macromolecular concept.[25] Macintosh applied rubber solutions between layers of fabric resulting in impermeable materials joined without stickiness. Hancock developed mastication where with repeated cutting, kneading and shredding, rubber became less elastic, more viscous and capable of flow due to the rupture of rubber molecules to produce materials of lower molecular weight. The Goodyear brothers crosslinked naturally occurring rubber, by treating it with sulphur. Vulcanised rubber, an elastomer, was produced by the addition of small amounts of sulphur and ebonite, a thermosetting plastic, by the addition of larger amounts. Schönbein reacted cellulose with nitric acid to produce cellulose nitrate, while celluloid was developed by the plasticizing of "cellulose di-nitrate" with camphor. These nitrates were replaced, by the discovery of cellulose acetate, a partially acetylated cellulose, known commercially as acetate rayon.

These early synthetic polymers were produced by the modification of naturally occurring polymers. Baekeland produced one of the first truly synthetic polymers, Bakelite, by reacting controlled amounts of phenols with formaldehyde to produce resins, from which were then produced the thermosetting plastics.

These scientists did not understand the concept of the polymer and it was not until the 1920`s that Staudinger[1] put forward the theory of the macromolecule as opposed to aggregates, cyclic structures or colloids as had been previously suggested. He proposed long chain structures for polystyrene, rubber and polyoxymethylene. His theory was backed up by x-ray studies and by the work of Carrothers on polyamides and polyesters, but it was not until Flory elucidated the chain reaction mechanism for polymer formation that the nature of the end groups in the macromolecules was understood.

After the concept of the macromolecule gained wide acceptance the number of synthetic polymers produced by both condensation and addition polymerisation reactions increased rapidly. The production of new polymers with increased performance by the discovery of new monomeric units, modification of existing polymers, by crosslinking reactions, improved polymerisation processes or copolymerisation with different monomer units continues to occupy the attention of large numbers of scientists to the present day.

An important area of polymer development is the addition of additives to many plastics to increase their stability or lifetime of practical use, or for aesthetic purposes. These plastics may have little practical use in their pure form or be unable to be processed without degrading and therefore

require modification to convert them into useful products. Additives used include fillers, for improved performance, colorants, anti-oxidants, flame retardants and various other stabilisers for increased stability and plasticizers to improve flow properties, to help in processing.

1.2 IONIC POLYMERS

Ionic polymers are polymeric materials, either organic or inorganic, containing both covalent and ionic bonds. From this definition the range of polymers, which includes both natural and synthetic substances, falling into this group is extensive.

In general terms the ionic bond is a strong bond, can be easily formed, under certain circumstances is thermally labile and it can show ion exchange properties in aqueous or molten salt form. All these characteristics can be utilised to form polymers with a range of useful properties.

The properties exhibited by these polymers range from rigid infusible or high melting solids through thermoplastics to viscous liquids. The rigidity will to a great extent be dependent on the number of ionic bonds that are present.

The structures of ionic polymers can be placed into three different categories.

(I) *Two or Three Dimensional Covalent Sheets or Networks which Contain Terminal Ionic Bonds.*

Examples of these derived from silica and a metal oxide are inorganic glass, sheet or network silicates, cement and clay products. Further

examples of networks are ion exchange resins, both cationic and anionic, based on functionalised crosslinked polystyrene.

(II) *Long Covalent Chains Containing Ionic Bonds.*

Examples of these are linear silicates which can be single or double stranded as in the asbestos type minerals, polyphosphates, ionomers, metal salts of polymers of acrylic and methacrylic acid, salts of carboxylated rubbers and polyelectrolytes.

(III) *Short Chain Segments with Metal Salt Bridges.*

These are di-carboxylic acids, for example sebacic acid, which are not polymers in the acid form but form chains because of salt bridges when ionised.

The work carried out for this thesis involves metal salts of acrylic acid. The systems studied include metal salts of poly(acrylic acid) and copolymers containing small amounts of metal carboxylate salts. Some examples of other polymers similar to this type of structure are given below.

Poly(acrylic acid) is a polyelectrolyte. These are polymers with ionisable side groups along the chain and may be a polyacid, polybase or polyampholyte. They exhibit properties in ionising solvents very different to non-ionisable structures.

Rigid, highly carboxylated ionic salt polymers are formed by the reaction of highly carboxylated polyacids, such as poly(acrylic acid) or poly(methacrylic acid). They can be formed in the solid state or in aqueous solution by acid-base reaction or the polymerisation of a metal acrylate.

The properties of these polymers depend greatly on the nature of the metal ion used. Monovalent cations, such as the alkali metals, produce water soluble polymers, unlike divalent metal salts which are highly crosslinked rigid structures.

Ionic polymer cements are used in dentistry and are the product of a hardening reaction, when polyacids, in particular poly(acrylic acid) is brought into contact with a simple metal oxide, such as zinc oxide.

The early research work carried out in the field of ionic polymers was mainly concerned with the use of ionic groups either to modify the properties of a given polymer or to achieve a new combination of properties. Early research was done by Brown[2] on carboxylated rubbers, by Nielsen[3] on the metal salts of poly(acrylic acid) and the Du Pont[4] company on ionomers.

Ionomers are generally classified as polymers consisting of a hydrocarbon backbone containing pendant carboxylic acid groups. The original ionomers were random copolymers of ethylene and methacrylic acid either partially or completely neutralised by sodium or zinc. Other ionomers can be formed from salts of acrylic acid with styrene.

The metal content in ionomers only amounts to a small fraction of the total weight. Ionomers are flexible, tough and truly thermoplastic even though the presence of divalent metal ions would be expected to promote some crosslinking. The crosslinks are labile at processing temperatures so these materials can be blow or injected moulded at melt temperatures as in the case of low density polyethylene. The upper temperature limit of use is restricted due to the labile nature of the ionic bonds at higher temperatures. The ionomers exhibit properties such as high transparency, toughness,

flexibility, adhesion and oil resistance which gives them desirable qualities e.g., as films in packaging.

Elastomers are polymers with high and rapid stretch capability, that have good tensile strength and high modulus when fully stretched and recover their original dimensions on the release of stress. The carboxylation of elastomers increases the inter- and intra- chain forces resulting in greater tensile strength but decreases extension and recovery properties of these polymers. These carboxyl groups were used by Brown to form sulphur free metal oxide crosslinks. The most widely used synthetic polymers were those based on butadiene, butadiene-styrene and butadiene-acrylonitrile systems.

1.3. POLYMER DEGRADATION

Polymer degradation causes changes in the physical properties of the polymer by chemical reactions involving bond scission principally of the macromolecule but also in pendant or side groups. These reactions lead to a reduction in molecular weight and chain length and lead to a deterioration of functionality. Modes of polymer degradation include mechanical, thermal, photochemical, radiochemical, biological and chemical.

For practical purposes polymeric materials must have a certain amount of durability, depending on the application, to make them useful. Over the course of time polymers may be susceptible in use to degradation by a number of factors such as weathering, mechanical or thermal fatigue, attack by micro-organisms or by the flammability of the polymer. Mechanical or thermal stress during processing can also cause degradation.

These processes reduce the useful lifetime of the polymer by affecting its physical properties or can cause some adverse aesthetic effect such as discoloration or loss of transparency of the polymer. It may be that a degradative process is desirable for a polymer, with recycling and/or disposal of long lived polymers becoming an environmentally important issue.

By gaining an understanding of the ways in which polymers degrade, under the above circumstances, it should be possible to select the appropriate polymer that gives the required performance. Alternatively, modification of the polymer by copolymerisation or by the addition of additives, such as flame retardants, anti-oxidants and light absorbers or excluders, are very important methods to help increase the stability of the polymer.

In this thesis the thermal stability and degradation of various polymer systems will be examined. The study of thermal degradation of polymers is important because as most polymers are organic molecules they will burn, if exposed to a high enough temperature. The resulting fire hazard is exacerbated in many cases by the production of large amounts of toxic fumes, responsible for a large proportion of fire deaths. By understanding how polymers degrade their suitability and safety can be evaluated.

The mechanisms for the thermal degradation of polymers can be split into two separate groups, namely depolymerisation and substituent reactions. The reaction mechanism can be radical or non-radical and the path followed depends on the chemical nature of the species involved.

(I) Depolymerisation

In depolymerisation, breaking of the polymer chains occurs at random with the products of degradation being similar to the original monomer unit. The presence of structural abnormalities such as peroxides, unsaturated terminal chain structures and chain branches, incorporated during polymerisation or processing are factors in decreasing the stability of polymers.

In poly(methyl methacrylate) chain scission is followed by depropagation with monomer being formed until the reaction is terminated by the combination of pairs of radicals or the end of the chain is reached.

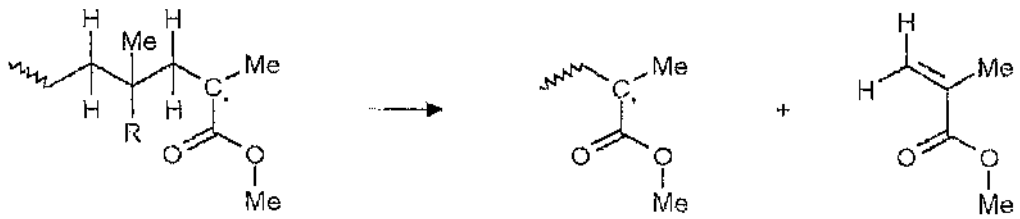


Fig 1.1 Depolymerisation of poly(methyl methacrylate).

In polyethylene little monomer is formed. Intermolecular transfer reactions produce long chain hydrocarbons, with smaller olefins being the result of intramolecular transfer.

The behaviour of polystyrene is intermediate between that of poly(methyl methacrylate) and polyethylene with both intramolecular transfer to give styrene oligomers and depolymerisation to give monomer occurring.

The type of reaction in these cases is dependent on the presence of an α–hydrogen atom. The absence of an α–hydrogen atom prevents transfer reactions so that depolymerisation is favoured as is seen when polystyrene is compared with poly-α-methylstyrene which undergoes almost complete depolymerisation to monomer.

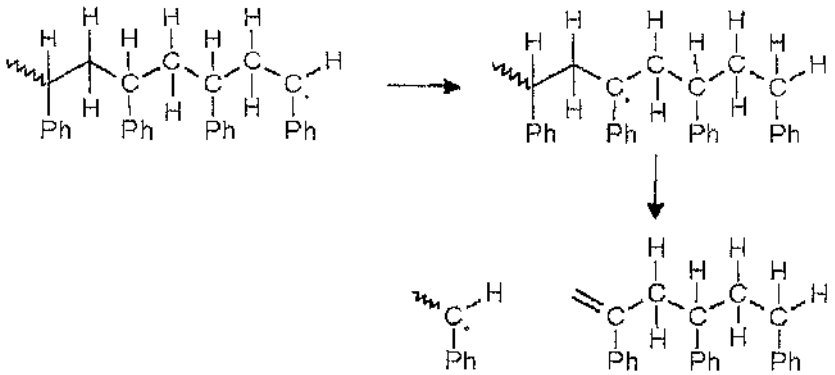


Fig. 1.2 Intramolecular transfer reaction in polystyrene.

If an α–hydrogen is present, a mixture of transfer and depolymerisation can occur, the favourability of each being determined by the ability of the other group on the carbon atom to stabilise the radical formed. The more stable the radical, the greater the amount of monomer formed, which is illustrated by comparing polystyrene with polyethylene.

(ii) Non Radical Depolymerisation

An example of non radical depolymerisation is the case of poly(dimethyl siloxane). The thermal degradation of this polymer results in cyclic oligomers, ranging from trimer to heptadecamer, as volatile products of degradation. The terminal hydroxyl groups are known to play some part in the degradation reaction as replacement of them with trimethylsilane groups increases the stability of the polymer while the addition of potassium hydroxide decreases the stability of the polymer. The reaction mechanism for the formation of trimer is illustrated in **Fig. 1.3**. The reaction of the hydroxyl group further from the chain end will lead to higher oligomers

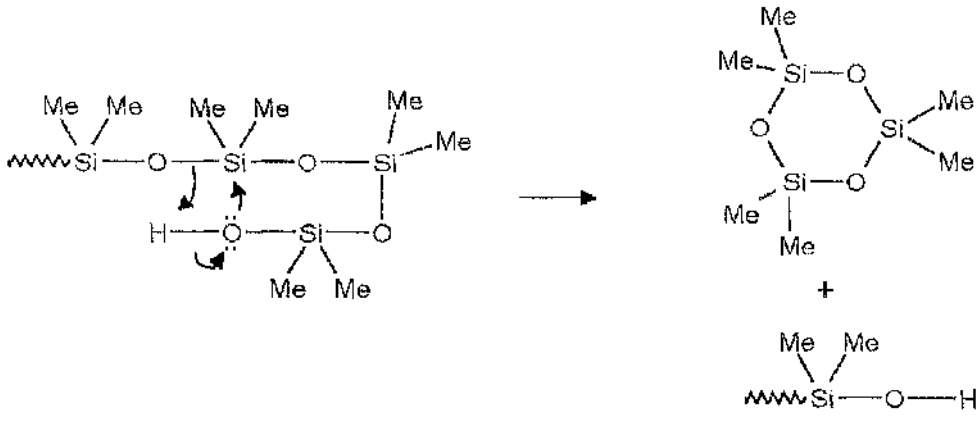


Fig 1.3 Mechanism of degradation of poly(dimethyl siloxane).

(iii) Substituent Reactions

In substituent reactions the structure of the repeat unit is altered although the main structure remains intact, with volatile products different from monomer being produced,

Examples of these are ester decomposition of some methacrylates where intramolecular hydrogen abstraction results in the formation of a methacrylic acid unit and the corresponding small alkene. The favourability of this reaction verses depolymerisation as seen for poly(methyl methacrylate) depends on the number of hydrogens present on the β-carbon atoms. Ester decompositions are favoured when greater numbers of β-hydrogen atoms are present and depolymerization is favoured for those with one or two β-hydrogen atoms.

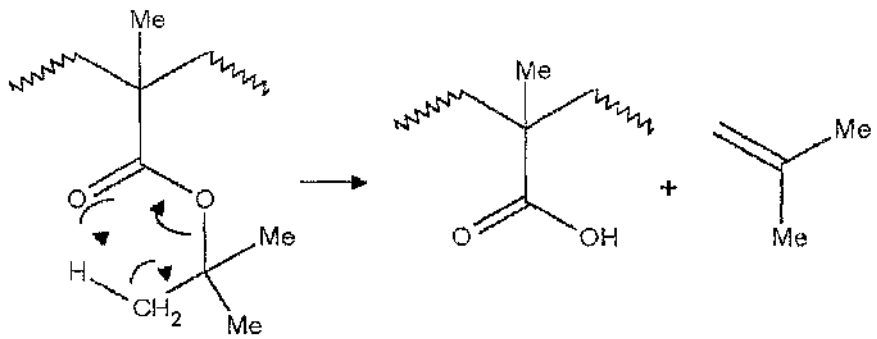


Fig 1.4 Intramolecular hydrogen abstraction resulting in side group scission in poly(t-butyl methacrylate).

Elimination reactions also occur with poly(vinyl chloride) and poly(vinyl acetate) where hydrogen chloride and acetic acid are lost to form conjugated chain structures and in poly(methacrylic acid), where intramolecular cyclisation occurs, with the elimination of water, to form acid anhydrides.

1.4. STUDY OF THERMAL DEGRADATION

A large number of methods are available for the study of the thermal properties of polymers and the nature of the chemical changes occurring therein. The methods used will depend on the information required and the mechanism by which the polymer degrades. No single method gives an overall picture of the degradation procedure, so it is desirable to use a number of complementary analysis techniques.

The change in molecular weight distribution of the polymer can be followed by viscometry, osmometry or gel permeation chromatography. This can be important when degradation occurs but there are no volatiles evolved or weight loss.

If there is a change in the number or kinds of functional groups in a polymer these can be observed using infra-red, ultra-violet or nuclear magnetic resonance spectroscopy.

The methods commonly used to study thermal degradation of polymers are differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG). These techniques give an indication that changes are taking place within the polymer but they do not show what the chemical changes are. Thermal volatilisation analysis (TVA), the technique used in this laboratory, analyses and identifies the products of degradation to help in the elucidation of the reaction mechanism.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES USED IN POLYMER DEGRADATION STUDIES

This chapter describes the methods involved and instrumentation used in study of the thermal degradation of the chosen polymers and subsequent analysis of the products of degradation.

As Thermal Volatilisation Analysis (TVA), along with the complementary SATVA technique, was utilised extensively throughout this work, a full description of the technique and the apparatus used is given below.

2.1 THERMAL VOLATILISATION ANALYSIS

Thermal volatilisation analysis (TVA) is a technique developed by M^{c}Neill and co-workers[5] to study the thermal degradation of polymers. When a polymer is heated in a continuously evacuated system, with a cold trap situated a certain distance away, a small pressure will develop due to the time taken for any volatile degradation products evolved to flow from the heated sample to the cold surface. The pressure in the system, which can be measured with a Pirani gauge, will be dependent on the rate of degradation and resulting rate of evolution of volatiles from the polymer (**Fig. 2.1**).

A TVA curve is a record of Pirani response versus temperature for a sample subjected to a linear increase of temperature with time, usually from ambient temperature to 500°C. The peaks found in the derivative of the TVA curve correspond to maxima in the rate of decomposition of the polymer.

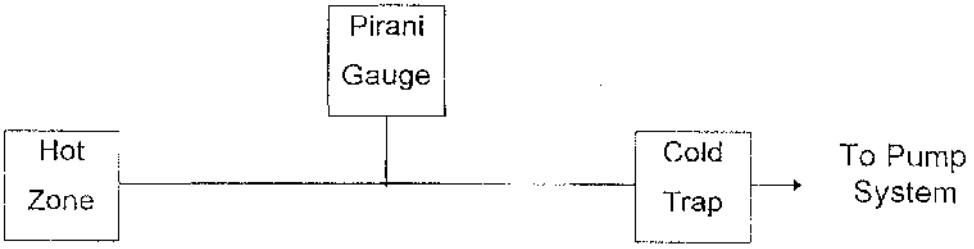


Fig. 2.1 Basic TVA system.

In TVA the cold trap is kept at -196°C by cooling with liquid nitrogen. This is sufficient to condense all the commonly found products of polymer degradation except gases such as carbon monoxide, hydrogen and methane. As a result of this, the importance of variation in the pumping speed in different systems is reduced.

2.1.1 Differential Condensation TVA

Differential condensation TVA[6] is a modification of the TVA technique which involves the addition of a trap before the Pirani gauge at a temperature higher than that of the original trap. By varying the temperature of this trap an indication of the range of volatility of degradation products can be gained, by comparing the change in pressure reading obtained as the temperature of the trap is altered.

To avoid repetition of a particular experiment the vacuum system can be split into separate parallel limbs each with a trap at a different temperature. During degradation the Pirani gauge responses are recorded simultaneously. This facilitates a comparison of the range of volatiles of the degradation products in a single experiment, as long as the distance from the sample to the main liquid nitrogen temperature trap is the same for each limb.

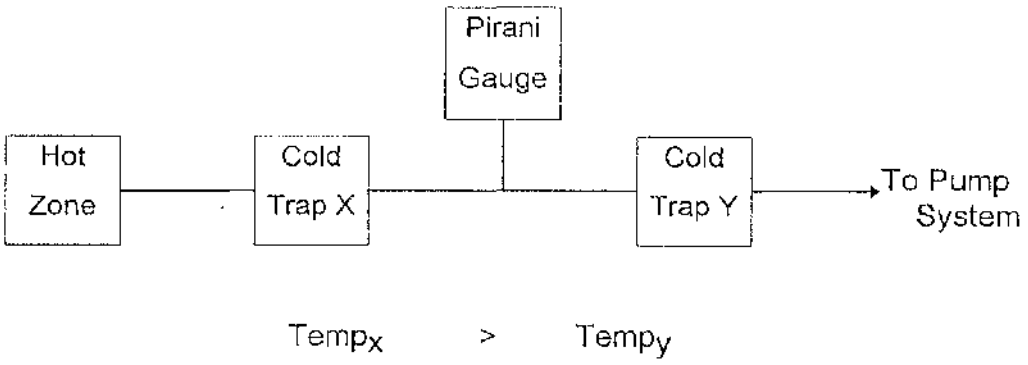


Fig 2.2 Differential condensation TVA system.

2.1.2 TVA Apparatus

A diagrammatic representation of the TVA vacuum line used is given in **Fig. 2.3** on page 18. The vacuum line is split into four separate limbs which are of the same length, each containing two U tube traps and a connection for a Pirani gauge. The most common temperatures of traps used in this laboratory are 0°C, -45°C, -75°C and -100°C, respectively. A Pirani gauge is placed after the liquid nitrogen trap to monitor the non-condensable gases evolved. The on-line mass spectrometer is used to identify the non-condensable gases produced.

It is desirable to have the sample under investigation as a thin film or finely ground powder. If the sample is too thick the degradation rate could be affected by the rate of diffusion of volatiles out of the polymer, or the degradation products could undergo secondary reactions giving misleading information about the reaction mechanism.

The samples are placed in a glass tube and heated in an adapted Perkin Elmer Model F11 gas chromatography oven, connected to a linear temperature controller (**Fig. 2.4,** page 19). The heating rate chosen for these experiments was 10°C per minute up to a temperature of approximately 500°C. The temperature in the oven is recorded by a K-type nickel-chromium/nickel-aluminium thermocouple, which is placed in the oven as close to the bottom of the sample tube as possible.

The tube, made from Pyrex glass contains a B40 cone, for connection by way of an adaptor to the vacuum line. It is 25 cm high with a base diameter of 3.5 cm and internal base area of approximately 9 $cm.^2$ As a result of this, the samples which in this study were between 60-80 mg in weight, could be spread thinly over the bottom of the tube. Water cooled condensers are placed either around the outside or inside the tube to condense the products volatile under vacuum at the elevated degradation temperatures but not volatile at room temperature. These products are called the cold ring fraction.

The system is evacuated prior to use down to a pressure of 10^{-4} torr, and is continuously evacuated during an experiment. The pump system used was an Edwards Speedivac ED100 oil diffusion pump backed up by an Edwards Speedivac 25C20A oil rotary pump.

The temperature of the sample is not measured directly. A good thermal contact is not always possible between an internal thermocouple and the sample and the sample might disappear during degradation. Another disadvantage of the internal thermocouple is that the metals of the thermocouple might affect the degradation process of the sample. In the TVA experiments the temperature recorded is that of the oven.

The sample temperature is always lower than that of the oven as there is a temperature gradient across the base of the degradation tube. The sample temperatures can be measured accurately by first calibrating the temperature of the base of the degradation tube against oven temperature. The difference in temperature between the oven thermocouple and the bottom of the inside of the sample tube can be measured by placing another K-type thermocouple inside the sample tube and recording the output of both thermocouples as the oven temperature is raised. A plot comparing the oven and tube thermocouple responses is shown in **Fig. 2.5** on page 20.

This has to be repeated for each sample tube to allow for any difference in the size, or the thickness of glass used in the tubes, or if the position relative to the thermocouple is changed. The temperatures quoted in the results have been adjusted to account for the results obtained in the calibration experiment.

2.1.3 Disadvantages in using TVA.

In TVA, the sample under investigation must evolve products of degradation volatile enough to be removed from the hot oven area to the vacuum line for detection by the Pirani gauges. The Pirani gauges will not detect any change in the system if the products are not volatile enough to be removed from the hot to the cold zone.

TVA will not give direct information about any changes to the physical properties of a polymer or structural changes in the polymer as it is being heated. TVA is used in conjunction with other analytical techniques to provide information about the processes taking place as the polymer is being heated.

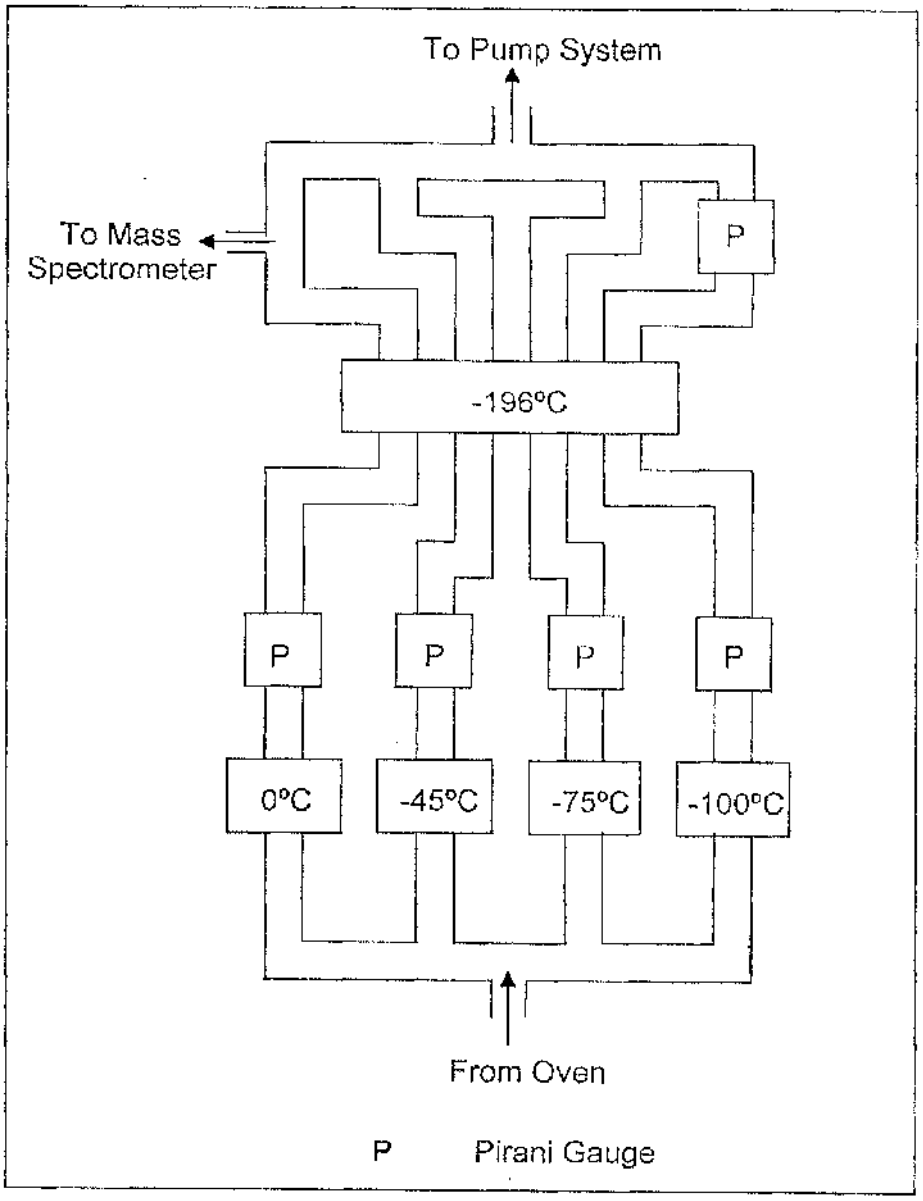


Fig. 2.3 Diagram of TVA system used.

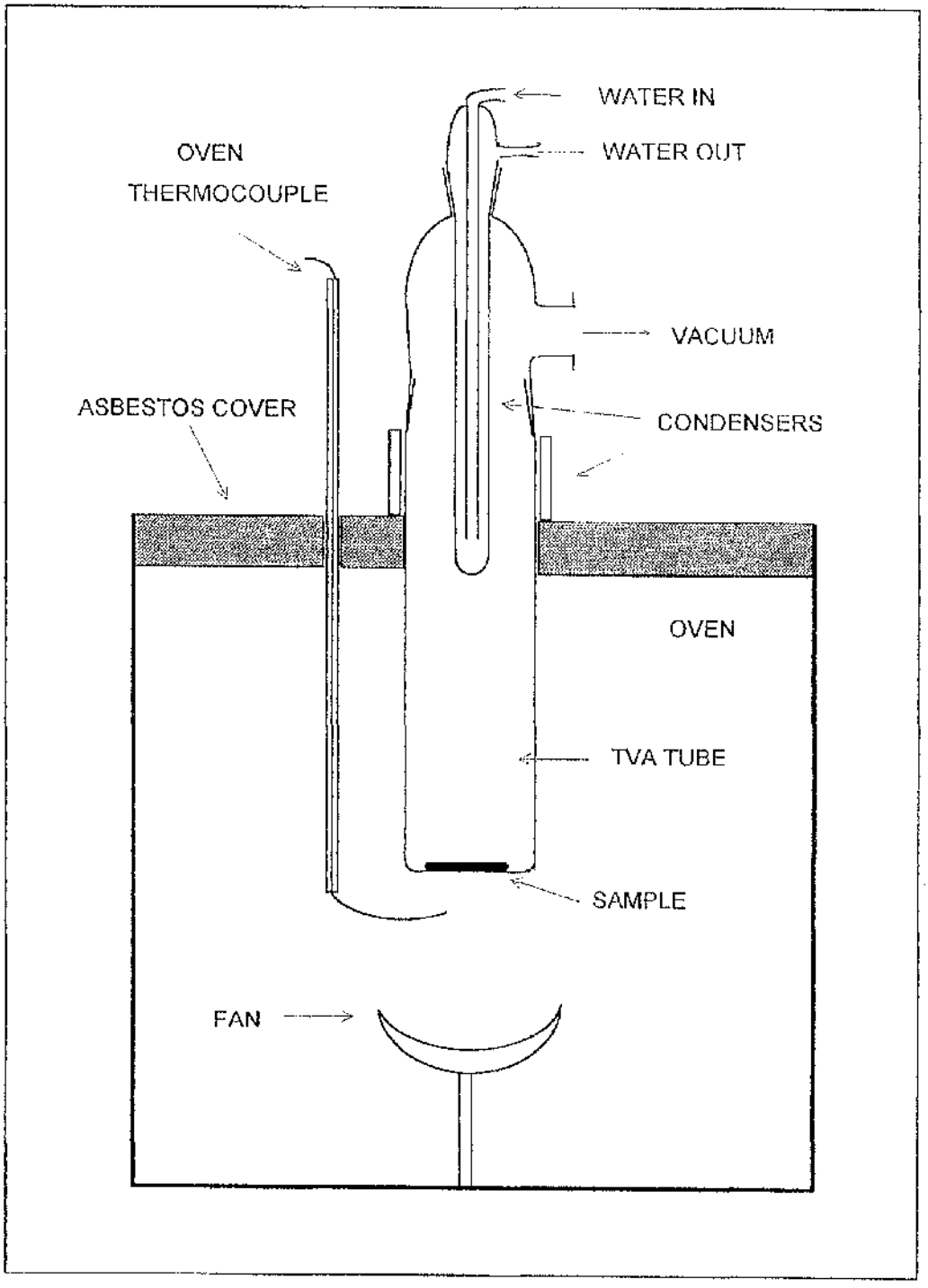


Fig. 2.4 TVA oven system.

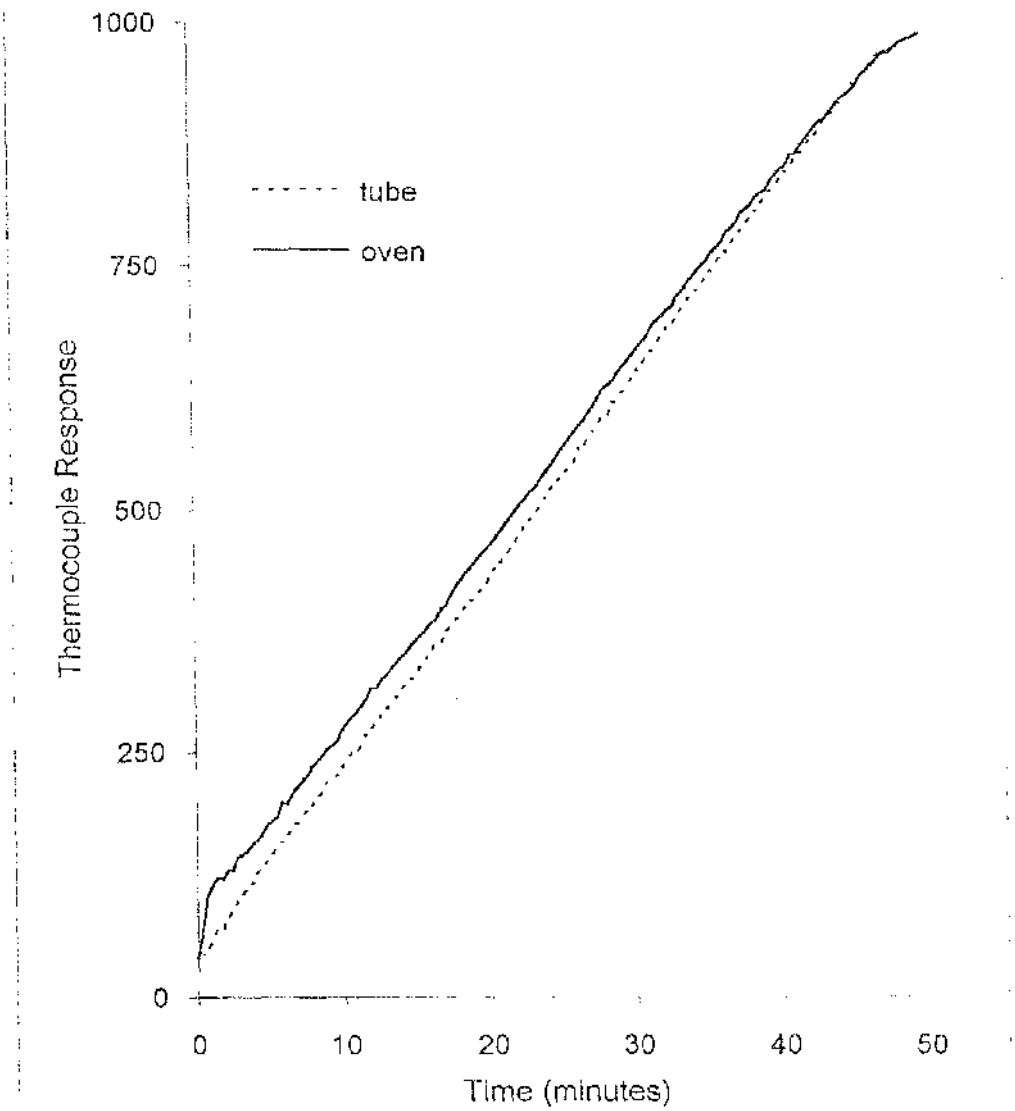


Fig. 2.5 Relative simultaneous response of a thermocouple in a TVA oven and of one touching the inside of a TVA tube during a programmed heating at 10°C/min in a TVA experiment.

2.2 *SUB-AMBIENT THERMAL VOLATILISATION ANALYSIS*

The results obtained from carrying out a TVA experiment provide information about the temperature and rate of evolution of volatile products of degradation and an indication of the range of volatility of these products. To be able to elucidate a mechanistic explanation for the degradation process it is first necessary to identify the products of degradation. The technique of sub-ambient thermal volatilisation analysis (SATVA) was developed by McNeill[7] to help in the separation, collection and identification of the degradation products evolved during the TVA experiment..

Before a SATVA separation all the condensed products from the TVA experiment are collected in a U tube trap surrounded by glass beads, cooled to -196°C by liquid nitrogen (**Fig. 2.7**). By shutting the stopcock after the trap, it is then possible to change the direction of pumping in the system to distil the degradation products back out of the trap in the opposite direction. They can then be collected as fractions in the vacuum line used for in TVA experiment.

Removal of the liquid nitrogen surrounding the trap, kept constantly under vacuum, results in a controlled slow warming up to ambient temperature, because of the surrounding glass beads. A partial separation of the products is achieved dependent on their volatility, with a longer warm up time enhancing separation of the products. The evolution of volatiles is monitored by the Pirani gauge and the readout of pressure obtained for within the system can be used as a guide in separating the various products. As in TVA the Pirani output is non-linear and is more sensitive at the low pressures of the scale.

The products are separated into fractions in different limbs by the successive opening and shutting of the pairs of taps on the vacuum line (Fig. 2.6), where they are collected for analysis in liquid nitrogen cooled traps. The pirani gauges connected to the limbs on the vacuum line are used to monitor distillation from the U tube traps to the collection points. Regular sampling of the volatiles during transfer, by a bleed to the on-line mass spectrometer, is also used in product identification, while there are two methods used, subsequent to the separation, for identifying those products collected in the traps.

The first method involves distilling the more volatile compounds from the traps into gas cells (**Fig. 2.8**) and recording their infra-red spectra The results obtained can be combined with the mass spectrometry results for identification purposes.

The gas cell consists of a B14 cone for connection to the vacuum line, a thin capillary tube in which the products are condensed, a greased glass tap to seal the cell and two sodium chloride windows transparent to the infra-red beam down to 600 $cm.^{-1}$

Depending on their number, the total separation of the less volatile degradation products is less likely to be achieved by SATVA. There is also often too small an amount of some substances for identification directly from the SATVA analysis techniques. These less volatile products are therefore often distilled *en masse* from a single trap into a liquid finger (Fig. 2.9). From this they are extracted in a suitable solvent and identified by GC-MS.

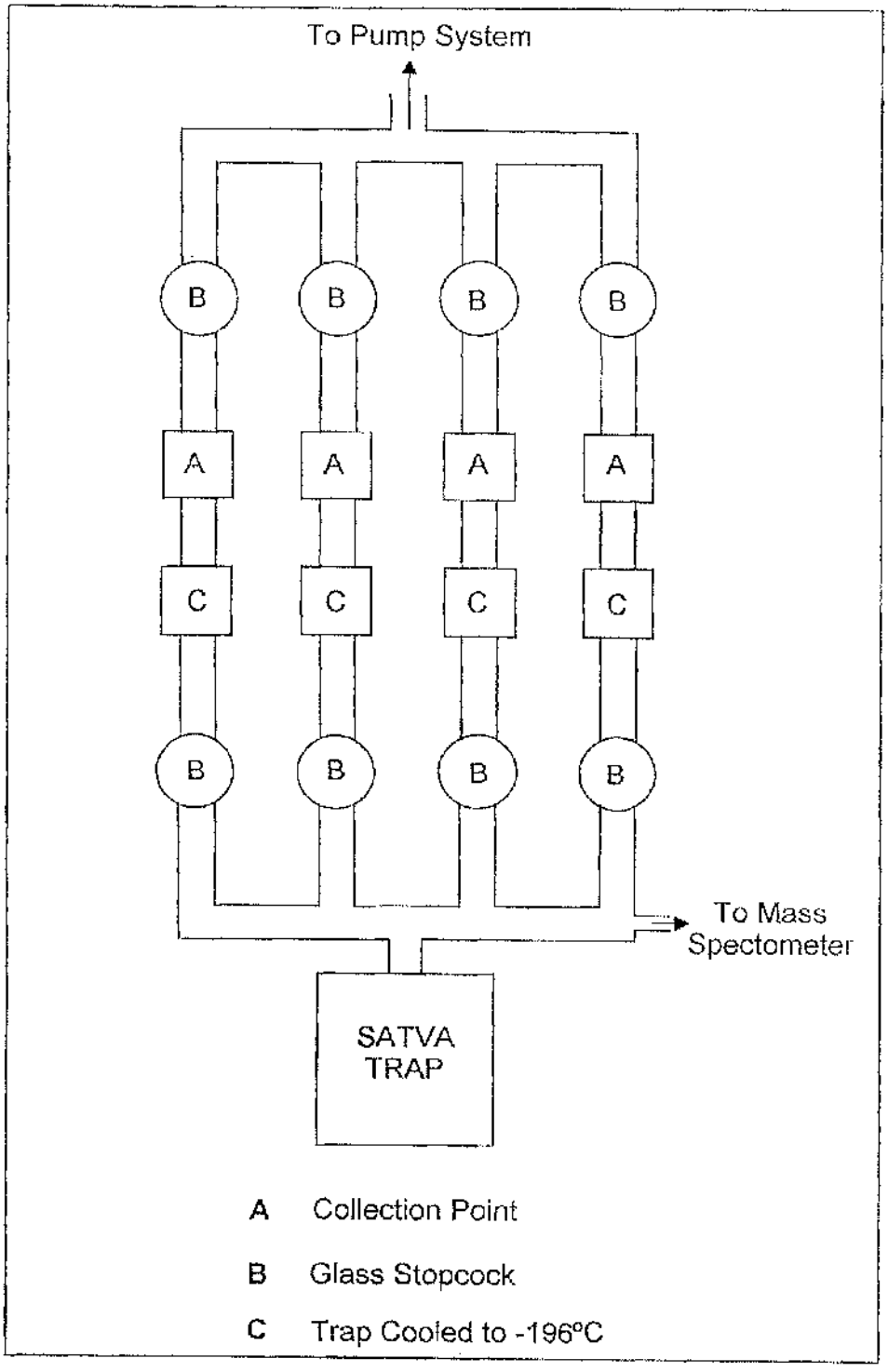


Fig. 2.6 Diagram of SATVA system.

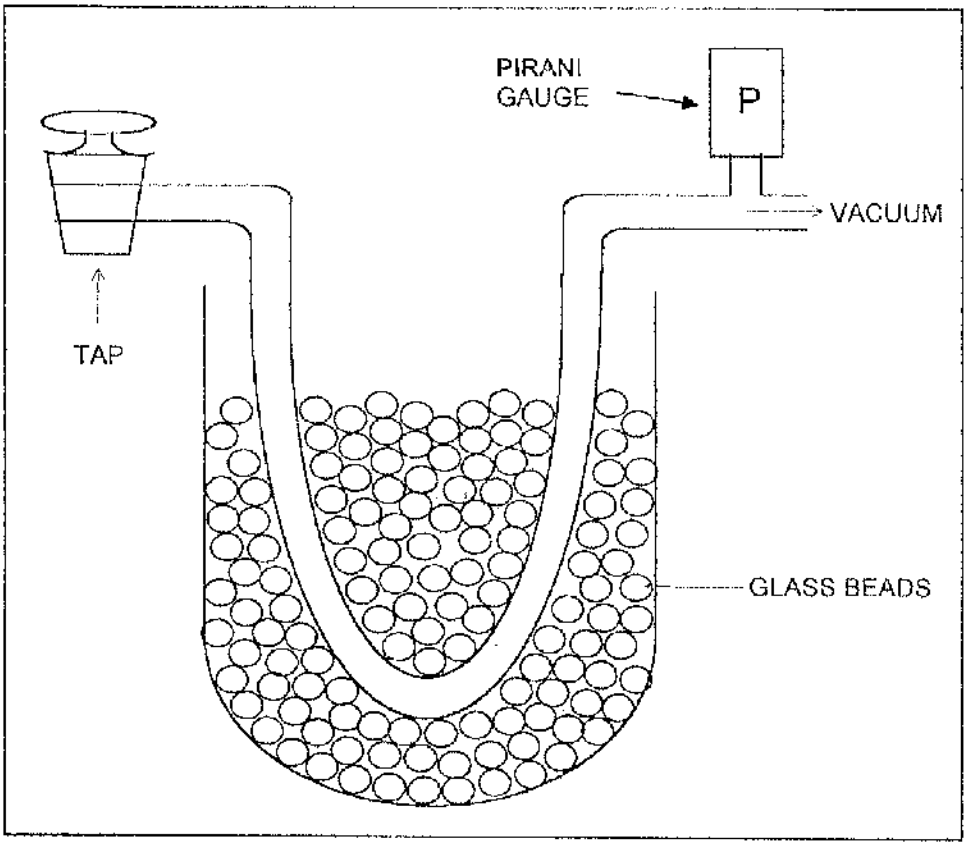


Fig. 2.7 SATVA trap.

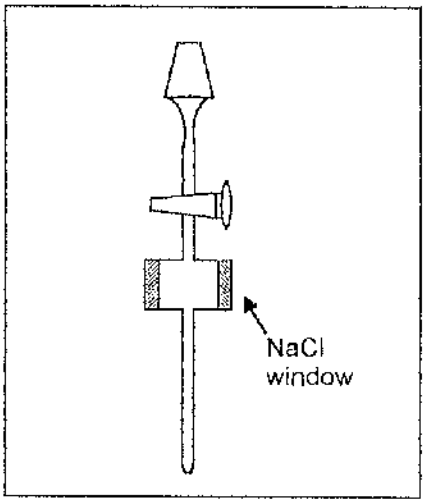


Fig. 2.8 Gas cell

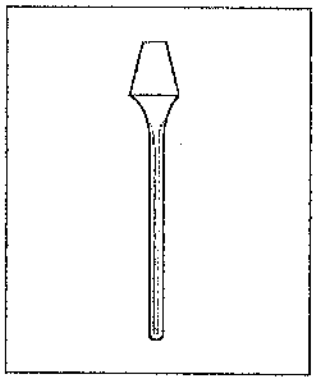


Fig. 2.9 Liquid finger

2.3 *DIFFERENTIAL SCANNING CALORIMETRY*

In DSC the sample under investigation and a reference are heated, in separate sample holders, at a predetermined rate. A temperature difference circuit compares the temperature of sample and reference and supplies power proportionately to a heater in each sample holder so that their temperatures remain the same. When the sample undergoes a thermal transition, the power to the two heaters is adjusted so that the temperatures of sample and reference remain the same. A signal proportional to the difference in power supplied is plotted as a function of temperature.

In this study the samples were heated under nitrogen flow of 50 ml/min at 10°C/min up to 500°C. The instrument used was a Du Pont 910 Differential Scanning Calorimeter interfaced to a Du Pont 9900 Computer/Thermal Analyser for data manipulation.

2.4 *DIFFERENTIAL THERMAL ANALYSIS*

In differential thermal analysis the sample and a reference, which does not undergo any thermal transition in the temperature range of study, are both heated at an identical rate. The temperature difference between the sample and reference is measured and plotted as a function of the sample temperature.

There is only a finite temperature difference between reference and sample when heat is being adsorbed or released due to endothermic or exothermic activity or a change in heat capacity of the sample occurs. Heat evolution in the sample is plotted upwards and heat absorption downwards.

In this study the samples were heated under nitrogen flow of 50 ml/min at 10°C/min up to 500°C. The instrument used in DTA was a Du Pont 900 Thermal Analyser with an alumina reference.

2.5 THERMOGRAVIMETRIC ANALYSIS

In thermogravimetry the sample is placed in a platinum sample pan which is hung on a sensitive silica rod balance. The weight of the sample is measured as it is heated either with linear rate of temperature increase, normally at 10°C/min, under a nitrogen flow of 50 ml/min, or isothermally, up to temperatures as high as 1500°C.

A plot of sample weight remaining as function of temperature is obtained. Also plotted is the derivative of the curve which is a function of the rate of weight loss in the sample with respect to temperature.

The instrument used for this work was a Du Pont 990 Thermogravimetric Analyzer.

2.6 INFRA-RED SPECTROSCOPY

The infra-red spectra of the monomers, polymers and degradation products were recorded as transmittance spectra on a Nicolet Magna Fourier Transform Infra-red System 550 Spectrometer with a scanning range from 4000 cm^{-1} to 400 $cm.^{-1}$

The metal containing monomers, polymers and degradation residues were analysed by grinding small amounts of sample with potassium bromide and pressing the mixture into discs using a pressure of 8 tons per square inch. The other copolymers and cold ring fractions were cast as films on sodium chloride plates by dissolving in dichloromethane, which was then allowed to evaporate to leave a thin sample film. Degradation products in the gaseous state were studied in the gas cells described in section 2.2.

2.7 GAS CHROMATOGRAPHY & MASS SPECTROMETRY

The GC-MS analysis of the degradation products was carried out on a Kratos MS 30 70V electron impact, medium resolution, double focus mass spectrometer coupled to a Perkin Elmer Sigma 3 gas chromatograph fitted with a 25 m dimethylsiloxane capillary column. For analysis the samples were dissolved in diethyl ether.

GC analysis was carried out on a Shimadzu GC 14A gas chromatograph fitted with a 30m 5% phenyl-95% dimethylsiloxane capillary column with C-R6A data processor.

The mass spectra of the cold ring fractions were recorded on a Kratos MS12 DS 70V, electron impact, low resolution, single focus mass spectrometer with a DS 55 data system.

The on-line mass spectrometer used in during TVA and SATVA experiments was a Leda Mass quadrapole mass spectrometer

2.8 GEL PERMEATION CHROMATOGRAPHY

The molecular weights of the copolymers of styrene with acrylic acid were estimated by of gel permeation chromatography.

Gel permeation chromatography is a separation method for high polymers. The separation takes place in a column filled with beads of a rigid, porous, highly crosslinked polystyrene or porous glass.

A dilute polymer solution is introduced into a solvent stream flowing through the column. As the polymer molecules flow past the beads they can diffuse into the pores to an extent depending on their size and pore-

size distribution. Larger molecules can enter only a small portion of the pores or are completely excluded while smaller molecules penetrate a larger number. As a result the larger molecules spend a shorter time in the column and are eluted more quickly.

Specific columns are calibrated empirically for retention time as a function of molecular size by narrow size range polymer samples, usually polystyrene.

Gel permeation chromatography was carried by Rapra Technology Limited. The analyses were carried out at ambient temperature using polystyrene gel, 30 cm 10 micron columns, with tetrahydrofuran as the solvent at a flow rate of 1.0 ml/min, with detection by a refractive index detector.

2.9 ELEMENTAL ANALYSIS

Elemental analysis of one milligram of sample was carried out after combustion in a CARLA-EBRA Elemental Analyser model 1106.

CHAPTER THREE

PREPARATION AND CHARACTERISATION OF MONOMERS AND POLYMERS

3.1 INTRODUCTION

This chapter describes the methods used in the preparation, purification and characterisation of monomers, polymers and copolymers containing transition metal salts of acrylic acid. The metals used for this study were cobalt, nickel, copper and zinc.

The first section deals with metal salt homopolymers of acrylic acid. Two different methods were used in the preparation of these polymers. The first method described includes the purification, preparation and characterisation procedures used in the synthesis of metal acrylate monomers and their subsequent polymerisation. The procedures followed are based on those described by Gronowski.[8] The second method of preparation involved the neutralisation of poly(acrylic acid) by the appropriate transition metal compound.

The final section of the chapter describes the methods used in the preparation of copolymers of styrene with acrylic acid and the subsequent attempted formation of zinc salts of these copolymers.

Metal salt polymers and copolymers based on methacrylic and acrylic acids have been prepared by a number of different methods both in solution and in the solid state. The metal salt can be formed by reaction of the appropriate metal compound with the acid monomer and subsequent

polymerisation or by reaction of a metal compound with the polymer or copolymer.

The reaction between the polymeric acid and metal salt has been carried out in both solution and the solid state. Neilsen[9] prepared the zinc salt of a 94/6 acrylic acid/2-ethylhexylacrylate copolymer by thoroughly mixing the copolymer with zinc oxide and moulding the powder at 300°C under high pressure. Zinc polyacrylate used as a dental cement is prepared by mixing an aqueous poly(acrylic acid) solution and zinc oxide into a paste with rapid hardening of the mixture occurring at oral temperatures.[10]

The formation of univalent metal polyacrylate salts can be achieved by the addition of metal oxide or hydroxide to an aqueous solution but the addition of divalent metal ions to aqueous solutions causes gelation to occur before complete neutralisation.

The solid state polymerisation of acrylates and methacrylates by gamma radiation has been studied by many workers.[11,12] The graft copolymerisation of nickel acrylate onto polyethylene has been examined as means of synthesis of a polymer supported catalyst.[13] Zinc acrylate has found use as a UV curable copolymer in scratch resistant floor coverings.[14] The impregnation of wood with metal acrylates and the subsequent polymerisation has been investigated as a means of improved fire resistance and dimensional stability.[15]

3.2 PREPARATION OF METAL ACRYLATE MONOMERS

The preparation of metal salts of acrylic or methacrylic acid and their subsequent polymerisation has been carried out by a number of workers.[16-18] Most of the work carried out on the preparation of these metal salts has involved metals of the first and second group with little research

done on the preparation of transition metal salt monomers and polymers until more recent years. Zulfiqar[19] synthesised the cobalt, nickel and copper salts of poly(methacrylic acid) by reacting the respective metal acetates with the sodium salt of poly(methacrylic acid). Most of the recent studies carried out on the preparation of transition metal acrylates have been based on the methods described by Gronowski.[8]

The monomers were prepared by the reaction of acrylic acid with the appropriate metal compound. The reaction of acrylic acid with the metal oxide or hydroxide as extensively used in the preparation of alkali and alkaline earth acrylates and methacrylates proved unsuccessful in the case of cobalt and nickel, so alternative compounds had to be found. The compounds used were zinc oxide, copper hydroxide, a basic cobalt carbonate and a basic nickel carbonate. Zinc oxide was used as supplied but the other three compounds had to be prepared prior to use.

3.2.1 Materials

Acrylic acid, zinc oxide, sucrose, sodium carbonate (Hopkin & Williams Ltd.); sodium hydroxide (Formachem Ltd); copper(II)sulphate (Riedel-de Haën Ltd); cobalt(II)chloride.$6H_2O$, nickel(II)nitrate.$6H_2O$ (Koch-Light Ltd); ammonia, zinc chloride, azobisisobutyronitrile, ethylenediaminetetraacetic acid, di-sodium salt (BDH Ltd).

3.2.2 Preparation and Purification of Starting Materials

3.2.2a Purification of acrylic acid

Acrylic acid has a boiling point of 141°C and it is supplied inhibited with 200 ppm hydroquinone monomethyl ether as inhibitor. To minimise the danger of polymerisation during distillation the acrylic acid samples were distilled at room temperature under high vacuum. The sample was first

degassed by three times freezing, with liquid nitrogen, and thawing, under high vacuum. The degassed monomer was then distilled into a vessel cooled to liquid nitrogen temperature, with the middle fraction being collected and used. Due to polymerisation during distillation, the rate of distillation decreased rapidly after approximately 40% of the sample had been distilled so the process was therefore halted at this point.

3.2.2b Preparation of Transition Metal Compounds

Basic Nickel and Cobalt Carbonates

To a well stirred approximately 0.1 M aqueous solution of nickel(II) nitrate.$6H_2O$ in distilled water was added an equal amount of anhydrous sodium carbonate. The resulting precipitate was stirred for a further 24 hours, washed repeatedly with distilled water and then dried, in a vacuum oven, at 60°C for 24 hours.

The same method as above was used in preparation of the basic cobalt(II) carbonate, with cobalt(II)chloride.$6H_2O$ used as the starting compound.

The metal content of these two compounds was found, by cheleometric titrations (section 3.3.1) to be 44.0% for nickel and 51.6% for cobalt. The molecular formulae for these compounds are $2Ni(OH)_2.NiCO_3.5H_2O$ and $2CoCO_3.Co(OH)_2.4H_2O$ respectively.

Copper(II)Hydroxide

During the reaction of copper(II)sulphate with an alkali metal hydroxide to form copper(II)hydroxide the formation of copper(II)oxide.H_2O also occurs. A small amount of sucrose was added to inhibit this reaction. To a stirred 0.5 M aqueous solution of copper(II)sulphate-5-hydrate in distilled water was added 0.2 g of sucrose and then dropwise a stoichiometric

amount of a 5 M aqueous solution of sodium hydroxide. The resulting precipitate was immediately and rapidly filtered, to minimise copper oxide formation, washed with distilled water and then dried in a vacuum oven at 60°C for 24 hours.

3.2.3 Monomer Preparation

Due to the high solubility of zinc acrylate in both methanol and water it was impracticable to isolate it from either of these solvents. The reactions of acrylic acid with the transition metal compounds were as a result carried out as suspensions in toluene. Due to the insolubility of both the starting metal salts and the metal acrylate products the reaction was carried out using excess acrylic acid to ensure the complete reaction of the starting material.

To a well stirred solution of acrylic acid (10-15% stoichiometric excess) in toluene, kept at a temperature between 40-50°C, was added zinc oxide, copper(II)hydroxide, basic cobalt(II)carbonate or basic nickel(II)carbonate over a period of 6 hours. Any water formed was removed as an azeotropic mixture with toluene. The resulting metal acrylates were filtered, washed with toluene and dried in a vacuum oven at 40°C for 48 hours, with the exception of nickel(II)acrylate which was filtered and washed with acetone before being dried.

3.3 MONOMER CHARACTERISATION

3.3.1 Metal Determination

The metal content for each monomer was calculated by cheleometric titrations of solutions of metal ions with a standardised solution of the di-

sodium salt of ethylenediaminetetraacetic acid (EDTA). These titrations were carried out with the appropriate indicator and at a suitable pH for the particular metal ion being studied.[20]

3.3.1a Preparation of Standardised EDTA Solution

An approximately 0.01 M EDTA solution was prepared by dissolving 3.7229 g of the EDTA di-sodium salt in distilled water and diluting to 1 L in a volumetric flask. The solution was standardised by titrating it against standard solutions of zinc and calcium ions until the results differed by less than 0.5%.

3.3.1b Determination of Cobalt, Nickel and Copper

The cobalt, nickel and copper salts of acrylic acid and the basic cobalt(II) and nickel(II) carbonates were accurately weighed in a porcelain crucible and then gently heated with a Bunsen burner until ignition, after which they were further heated until only the metal oxide remained. The residue was dissolved in a few drops of hot hydrochloric acid (AR Grade) and then transferred to a 100 ml volumetric flask and diluted to the volume by the addition of deionised water.

To 10ml portions of this solution was added a small amount of murexide indicator and then a few drops of concentrated aqueous ammonia until the solution turned yellow. It was then titrated with the standardised 0.01 M EDTA solution until the end point indicated by the appearance of a pink colour.

3.3.1c Determination of Zinc

The same method was used as above except after transferring to the volumetric flask 7.0 g of NH_4Cl and 57 ml of concentrated aqueous ammonia were added and the solution diluted to the volume with deionised water.

To 10 ml portions of this solution were added a few drops of Eriochrome Black T indicator and the solution was titrated with the standard 0.01 M EDTA until the colour of the solution changed from red to blue.

The percentage metal content, calculated and found for each monomer is given in **Table 3.1** below.

Monomer	% Calculated	% Found
Zinc Acrylate	31.5	31.1
Copper Acrylate	30.9	30.3
Nickel Acrylate	29.2	28.1
Cobalt Acrylate	29.3	28.8

Table 3.1 Metal content of monomers.

3.3.2 Carbon and Hydrogen Content of Monomers

The carbon and hydrogen contents for each monomer were found by microanalysis, with the use of a Carlo Ebra Elemental Analyser Model no. 1106. The results are given in **Table 3.2**.

Monomer	% Carbon		% Hydrogen	
	Theory	Found	Theory	Found
Zinc Acrylate	34.74	34.74	2.89	2.87
Copper Acrylate	35.04	34.34	2.95	2.85
Nickel Acrylate	35.88	31.55	3.01	3.78
Cobalt Acrylate	35.74	33.25	3.01	3.11

Table 3.2 carbon and hydrogen content of monomers

From the results obtained for metal, carbon and hydrogen content the empirical formulae can be calculated and compared to the theoretical values calculated for the monomers.

The amount of oxygen in each monomer was calculated from the remaining mass percentage after subtraction of the metal, carbon and hydrogen content. This may be a source of error as it will include any

resulting from the visual estimation of the end-point in the metal-EDTA titrations.

The elemental analysis for zinc acrylate gave the following results: Zn=31.1%, C=34.74%, H=2.87% and O=31.3%. These are in agreement with the theoretical values for the molecular formula $ZnC_6H_6O_4$, where Zn=31.51%, C=34.74%, H=2.89% and O=30.83%

The elemental analysis for copper acrylate gave the following results: Cu=30.3%, C=34.34%, H=2.85% and O=32.51%. These are in agreement with the theoretical values for the molecular formula $CuC_6H_6O_4$, where Cu=30.90%, C=35.04%, H=2.95% and O=31.11%.

The elemental analysis for nickel acrylate gave the following results: Ni=28.1%, C=31.55%, H=3.78% and O=36.57%. These results are not in agreement with the theoretical values for the molecular formula $NiC_6H_6O_4$, where Ni=29.22%, C=35.88%, H=3.01% and O=31.87%, but correspond to the formula $NiC_6H_8O_5$.

The elemental analysis for cobalt acrylate gave the following results: Co=28.8%, C=33.25%, H=3.11% and O=34.84%. These results are not in agreement with the theoretical values for the molecular formula $CoC_6H_6O_4$, where Co=29.32%, C=35.74%, H=3.01% and O=31.82%, but correspond to the formula $CoC_6H_7O_{4.5}$.

The difference in the theoretical and calculated values in elemental analysis for the nickel and cobalt acrylates can be attributed to the presence of water in these monomers. This will explain the greater than expected hydrogen and oxygen content. The results for the empirical

formulae for nickel and cobalt acrylate are consistent with the formulae $NiC_6H_6O_4.H_2O$ and $CoC_6H_6O_4.½H_2O$, respectively.

3.3.3 Infra-red Spectra of Monomers

The monomers were prepared for infra-red analysis by first dissolving a small amount of the solid sample in methanol and dropping the resulting solution on to a sodium chloride plate. The methanol solvent was then evaporated off under a drying lamp which resulted in a thin layer deposit of sample remaining on the sodium chloride plate. The infra-red spectra obtained for the four monomers are shown in **Fig. 3.1(a)** to **(d)**. The peak assignments are similar for all of the four monomers.

The main bands of interest in the spectra of the metal acrylates that will distinguish them from the corresponding polymers, are the olefinic C-H stretching bands between 3000 cm^{-1} and 3100 $cm.^{-1}$ the C=C double bond stretch at 1640 cm^{-1} and olefinic C-H out of plane deformations below 1000 $cm.^{-1}$ The carboxylate anti-symmetrical and symmetrical stretches are at 1565 cm^{-1} and 1443 cm^{-1} respectively.

3.4 POLYMERISATION OF MONOMERS

The free radical polymerisations of the metal acrylate monomers were carried out in methanol solutions at 60°C, with azobisisobutyronitrile (AIBN) as initiator, in the absence of air.

The reaction vessels were Pyrex glass dilatometers (**Fig. 3.2**) provided with a B14 cone for connection to a vacuum line and a constriction to allow sealing by heating under vacuum.

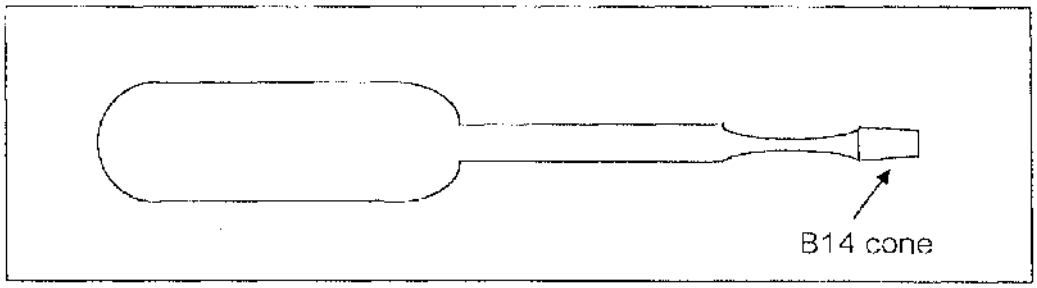


Fig 3.2 Dilatometer used in polymerisations

3.4.1 Purification of Materials

3.4.1a Drying of Methanol

Methanol (AR Grade) was dried over anhydrous magnesium sulphate for 48 hours and then overnight with calcium hydride before distillation, with the middle fraction being collected and used immediately.

3.4.1b Purification of Azobisisobutyronitrile

AIBN was purified prior to use, by first dissolving it in warm methanol and filtering off any insoluble particles. Recrystallisation from solution occurred at room temperature; the crystals were filtered and dried under vacuum at 20°C for four hours and stored in a refrigerator.

3.4.2 Polymerisation Procedure

The dilatometers were calibrated by the addition of known amounts of acetone. They were cleaned by washing successively with Pyroneg soap solution, distilled water and acetone (AR grade), before being flamed out by gentle heating under vacuum.

To a dilatometer of known volume was added, in turn, the initiator, the monomer and finally the appropriate volume of the methanol solvent. The resulting solution was degassed on a vacuum line by repeated freezing and thawing until the pressure in the vessel was reduced to 10^{-3} torr after which it was sealed.

The polymerisations were carried out in a constant temperature water bath, the temperature of which was programmable to an accuracy of 0.1°C. After the desired time the resulting precipitated polymer was filtered out of the reaction mixture and washed repeatedly with methanol. It was initially dried in a vacuum oven at 60°C for 48 hours and then at 40°C for 7 days.

The monomer and initiator concentrations, reaction time and the % conversion for each of the polymers is given in **Table 3.3**

	monomer conc g/dl	initiator conc.g/dl	reaction time hours	% conversion
zinc acrylate	7.10	0.05	0.25	42.91
cobalt acrylate	7.24	0.35	4.00	51.03
nickel acrylate	6.26	0.32	5.00	49.38
copper acrylate	8.35	0.68	50.00	4.10

Table 3.3 Polymerisation data for metal acrylate monomers.

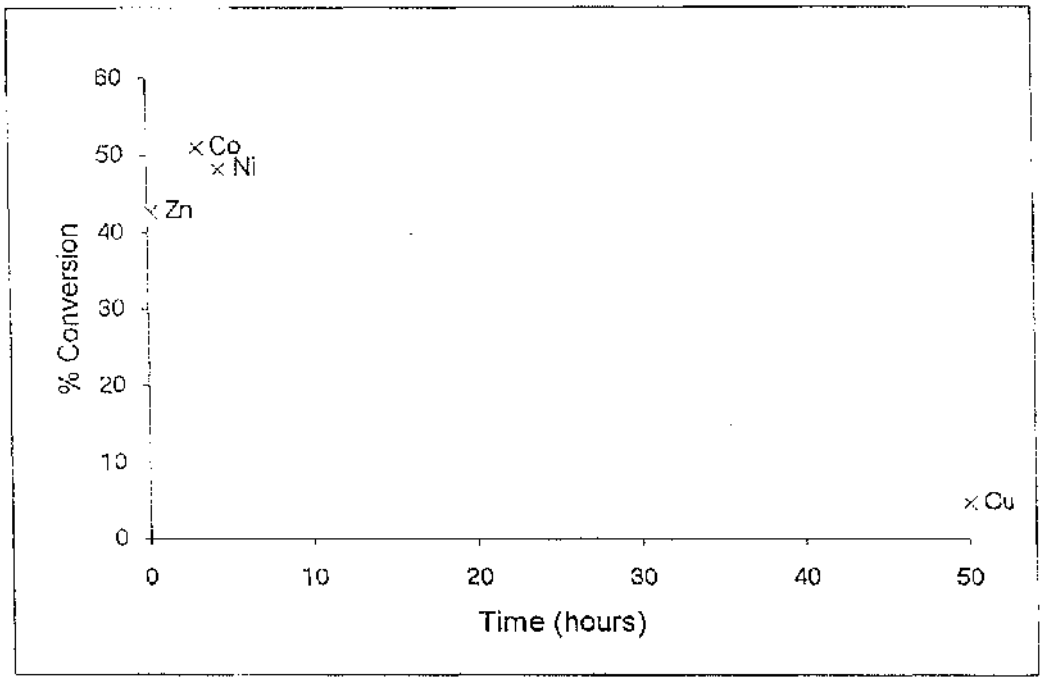


Fig. 3.3 % Conversion of metal acrylate monomers

The rate of polymerisation was greatly influenced by the metal ion involved. The rate of polymerisation of zinc acrylate was much greater than that of either cobalt or nickel acrylate. Zinc acrylate (**Fig. 3.3**) achieved a 42.9% conversion in a time of 15 minutes, compared to conversions of approximately 50% for the cobalt and nickel acrylates in times of 4-5 hours, using between five and six times the initiator concentration. Copper acrylate displayed an extreme reluctance to polymerise. The extent of conversion was only 4.1% after 50 hours despite having a slightly greater monomer concentration and approximately 12.5 times the concentration of initiator used in the polymerisation of zinc acrylate.

3.4.3 Infrared Spectra of Polymers

The infra-red spectra of the polymers were recorded using samples pressed, under high pressure into KBr disks. The spectra for the zinc cobalt, nickel and copper polyacrylates are given in **Figs. 3.4 (a), (b), (c)**

and **(d)** respectively. These spectra still contained an absorption at approximately 1640 cm^{-1} appearing as shoulder on the carboxylate absorption which is due to the presence of unreacted C=C double bonds in the polymers because of the di-vinyl nature of the monomer. Repeated washing of the polymers did not remove this band which reduces the possibility of unreacted monomer being the cause of this absorption. The number of these groups present in the polymers was not calculated.

The infrared spectra no longer contained the olefinic C-H bands between 3000 cm^{-1} and 3100 cm^{-1} but the carboxylate anti-symmetrical and symmetrical stretches were present at 1560 cm^{-1} and 1440 $cm.^{-1}$

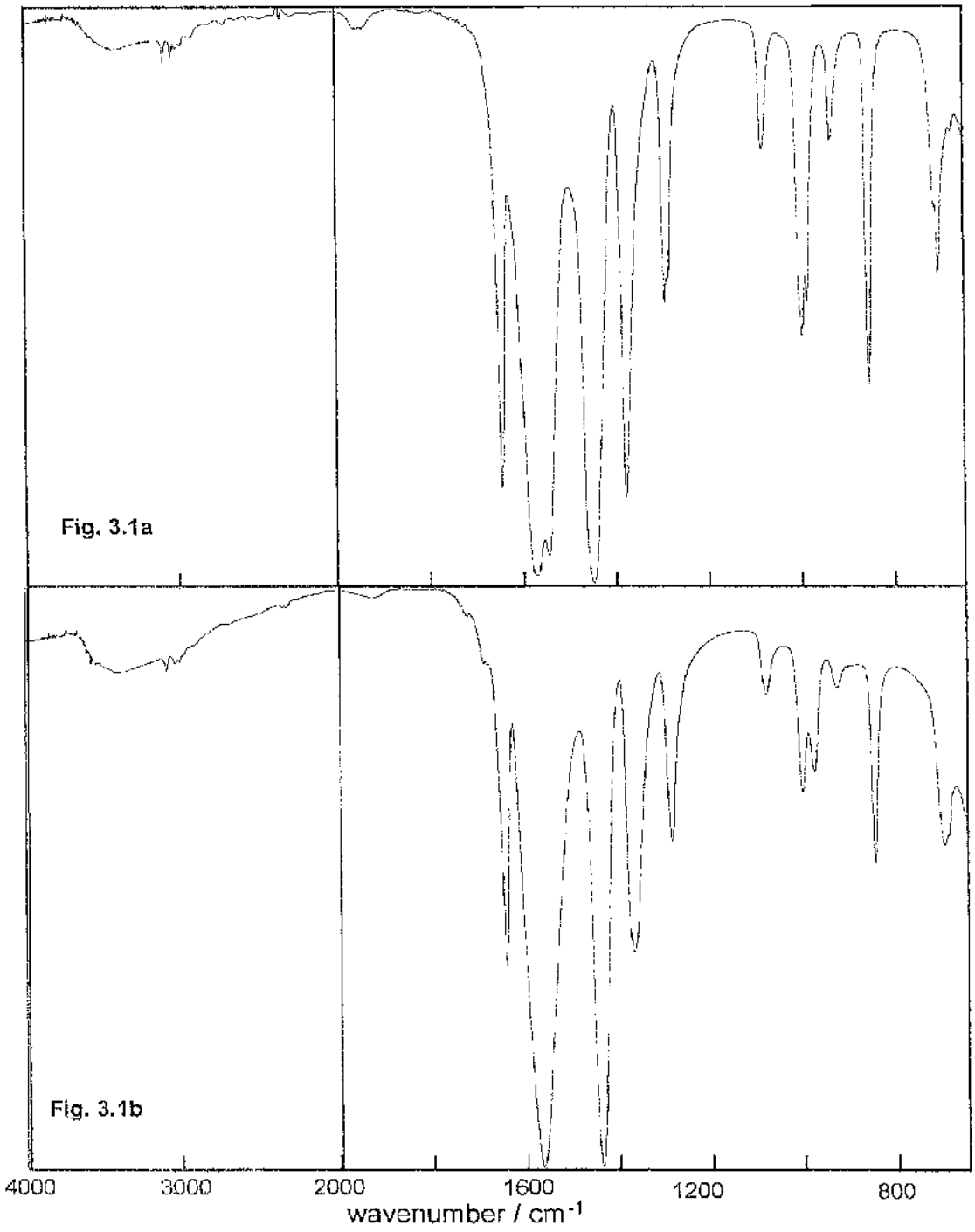


Fig. 3.1a Infra-red spectrum of zinc acrylate.

Fig. 3.1b Infra-red spectrum of cobalt acrylate.

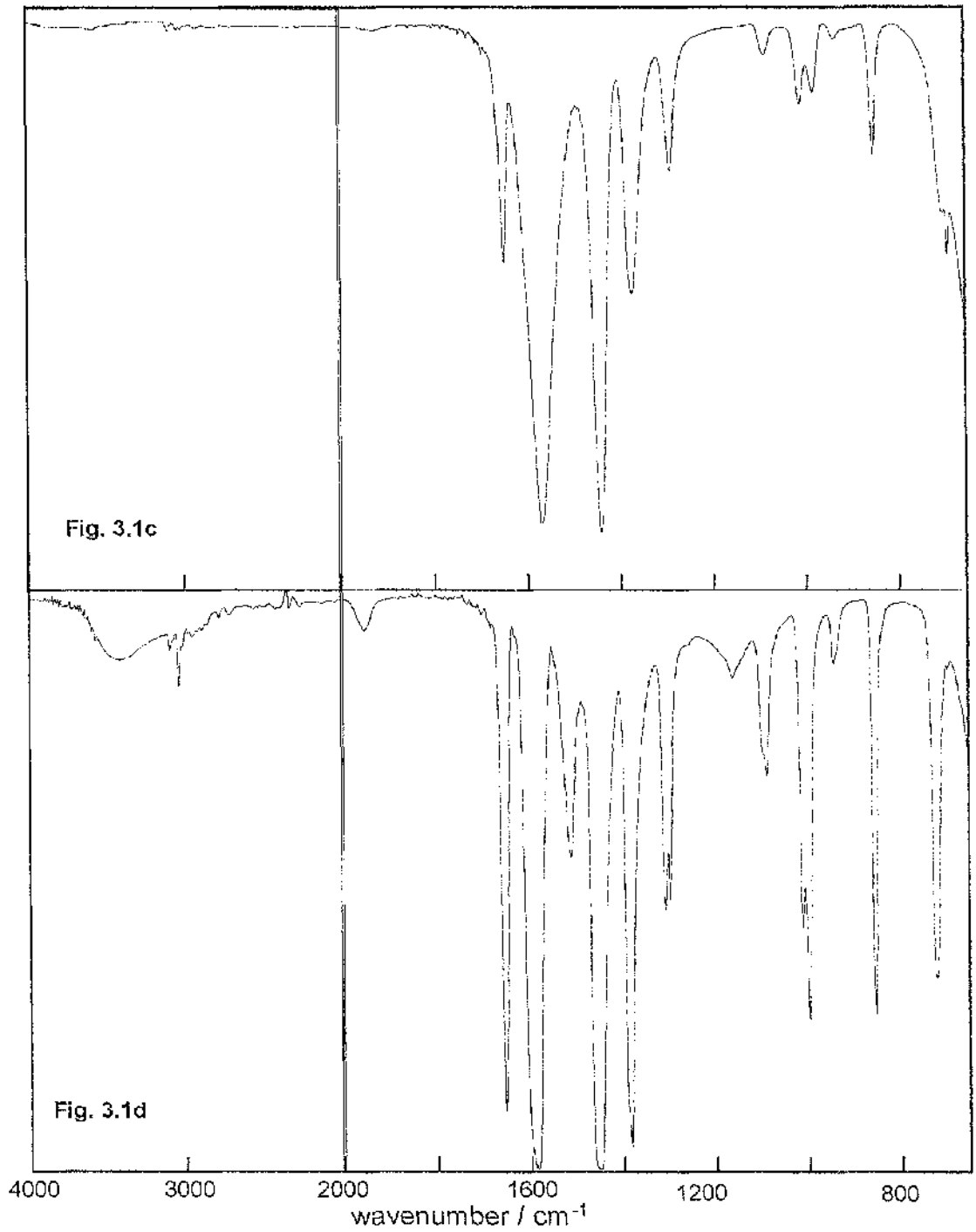


Fig. 3.1c Infra-red spectrum of copper acrylate.

Fig. 3.1d Infra-red spectrum of nickel acrylate.

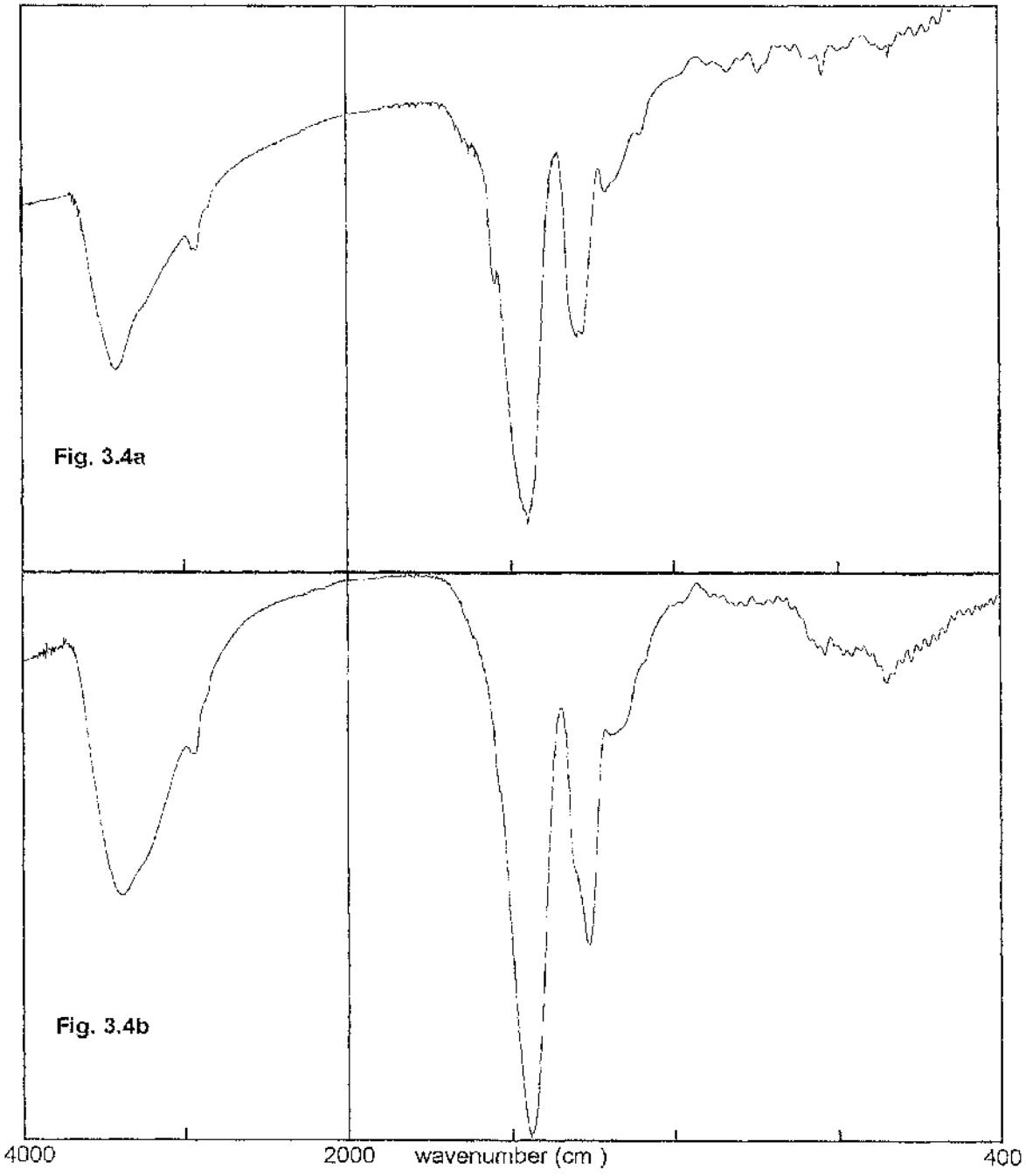


Fig. 3.4a Infra-red spectrum of zinc polyacrylate*.

Fig. 3.4b Infra-red spectrum of cobalt polyacrylate*.

* made by polymerisation

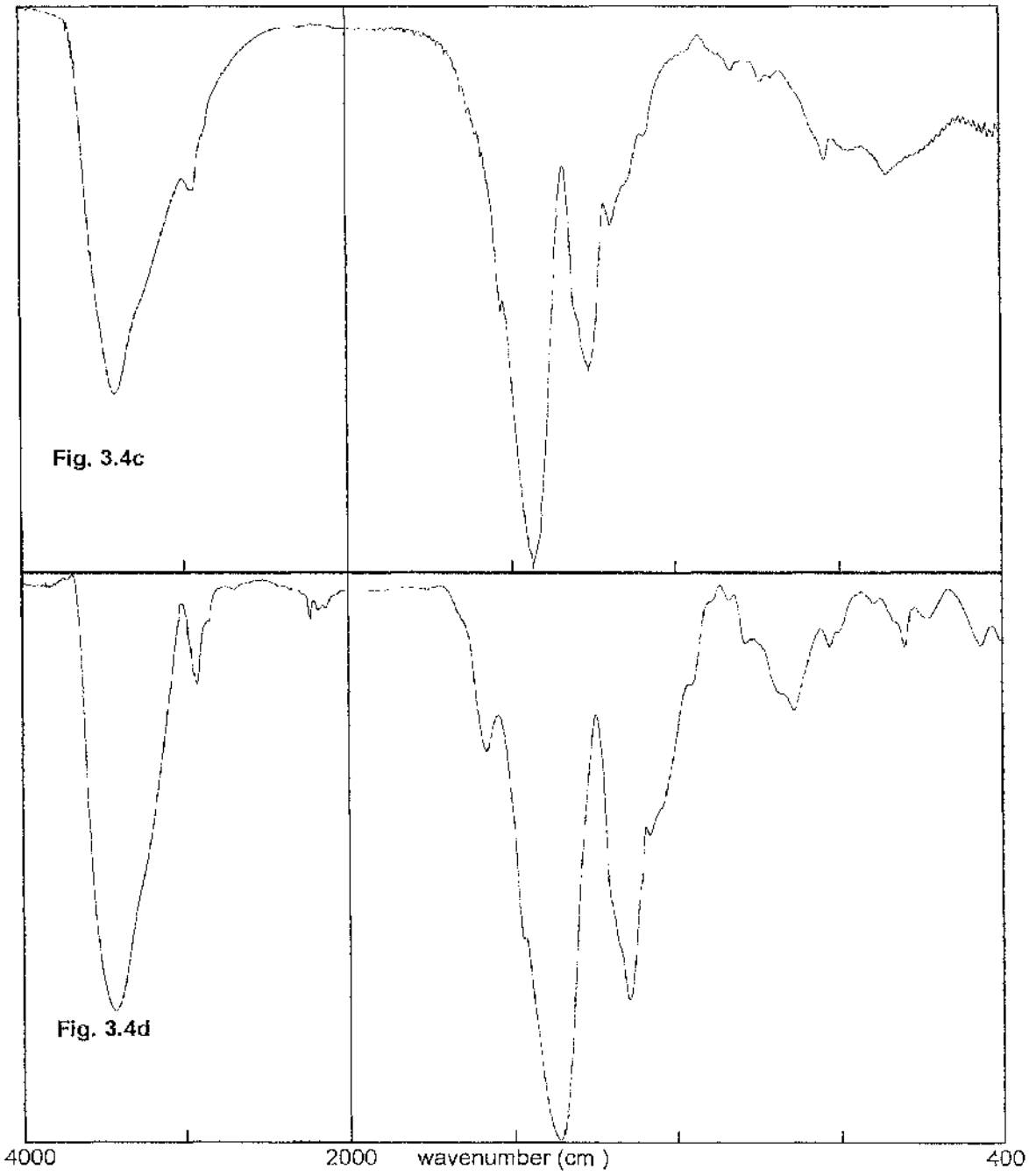


Fig. 3.4c Infra-red spectrum of nickel polyacrylate*.

Fig. 3.4d Infra-red spectrum of copper polyacrylate*.

* made by polymerisation

3.5. *PREPARATION OF POLYACRYLATE SALTS BY NEUTRALISATION OF POLY(ACRYLIC ACID)*

The metal polyacrylate salts made by neutralisation of poly(acrylic acid) were synthesised by reacting a commercially produced sample of poly(acrylic acid) with an average molecular weight of 2,000 with the same metal compounds used in section 3.2.3 in monomer preparation. An attempt to synthesise the polyacrylates using a poly(acrylic acid) with an average molecular weight of 90,000 proved unsuccessful as large lumps of a mixture containing precipitated polyacrylate and starting metal compounds formed which could not be purified.

3.5.1 Materials

Poly(acrylic acid) average molecular weight 2,000, 25% aqueous solution (Aldrich Chemical Company).

3.5.2 Procedure

To a well stirred aqueous solution of poly(acrylic acid) was gradually added small amounts of the transition metal compounds, until the formation of the insoluble polyacrylate salts occurred. These were then filtered out of the reaction mixture, washed three times with distilled water and dried in a vacuum oven at 60°C for 72 hours.

3.5.3 Characterisation

The metal contents of the polymers were calculated by the methods used in section 3.2 and are given in **Table 3.5.** The values obtained for the zinc, nickel and copper salts are less than the calculated theoretical values. This could be attributed to the precipitation out of solution of the insoluble polymers before complete neutralisation and the presence of water complexed to the metal ion as was found in some of the monomers, or of

residual water in the polymer, due to their highly crosslinked nature, even after prolonged drying.

The infra-red spectra of the polymers (**Figs. 3.5 (a)** to **(d)**) are similar to those obtained for the polymers made by polymerisation, but the band at 1640 cm^{-1} due to the unreacted carbon-carbon double bond is absent.

The low metal content in the copper polymer is also indicated from the infra-red spectrum, showing a strong absorption at 1713 cm^{-1} due to unreacted carboxylic acid groups. This band though much weaker is also present in the spectra of the other three polymers.

A difference in position of the anti-symmetrical carboxylate stretch is seen for copper polyacrylate from those of the other three metal polyacrylates. The main absorption for the anti-symmetrical carboxylate absorption, in copper polyacrylate is found at 1616 $cm,^{-1}$ with a shoulder at 1556 $cm.^{-1}$ The absorption at 1616 cm^{-1} is characteristic of bridging carboxylate structures, while the absorption at 1556 cm^{-1} is characteristic of chelates around metal ions.

In the cases of the other three metal ions the main carboxylate anti-symmetrical absorption is at 1550 $cm,^{-1}$ which would indicate the predomminance of metal chelates.

Polymer	% Metal Content	
	Theory	Found
zinc polyacrylate	31.5%	27.0%
cobalt polyacrylate	29.3%	31.8%
nickel polyacrylate	29.2%	25.8%
copper polyacrylate	30.9%	19.9%

Table 3.5 Metal content of polymers made by neutralisation.

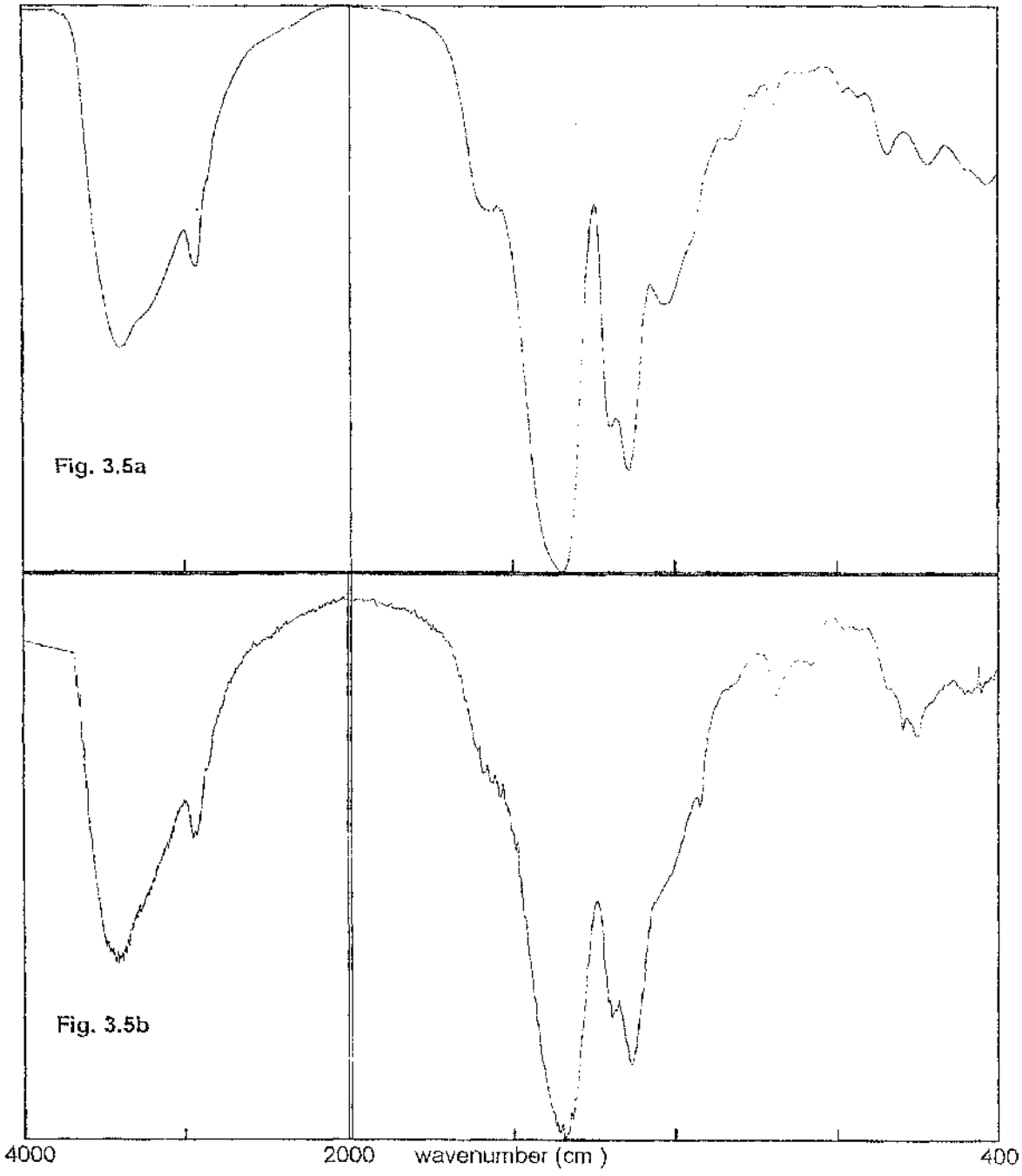


Fig. 3.5a Infra-red spectrum of zinc polyacrylate*.

Fig. 3.5b Infra-red spectrum of cobalt polyacrylate*.

* made by neutralisation of poly(acrylic acid)

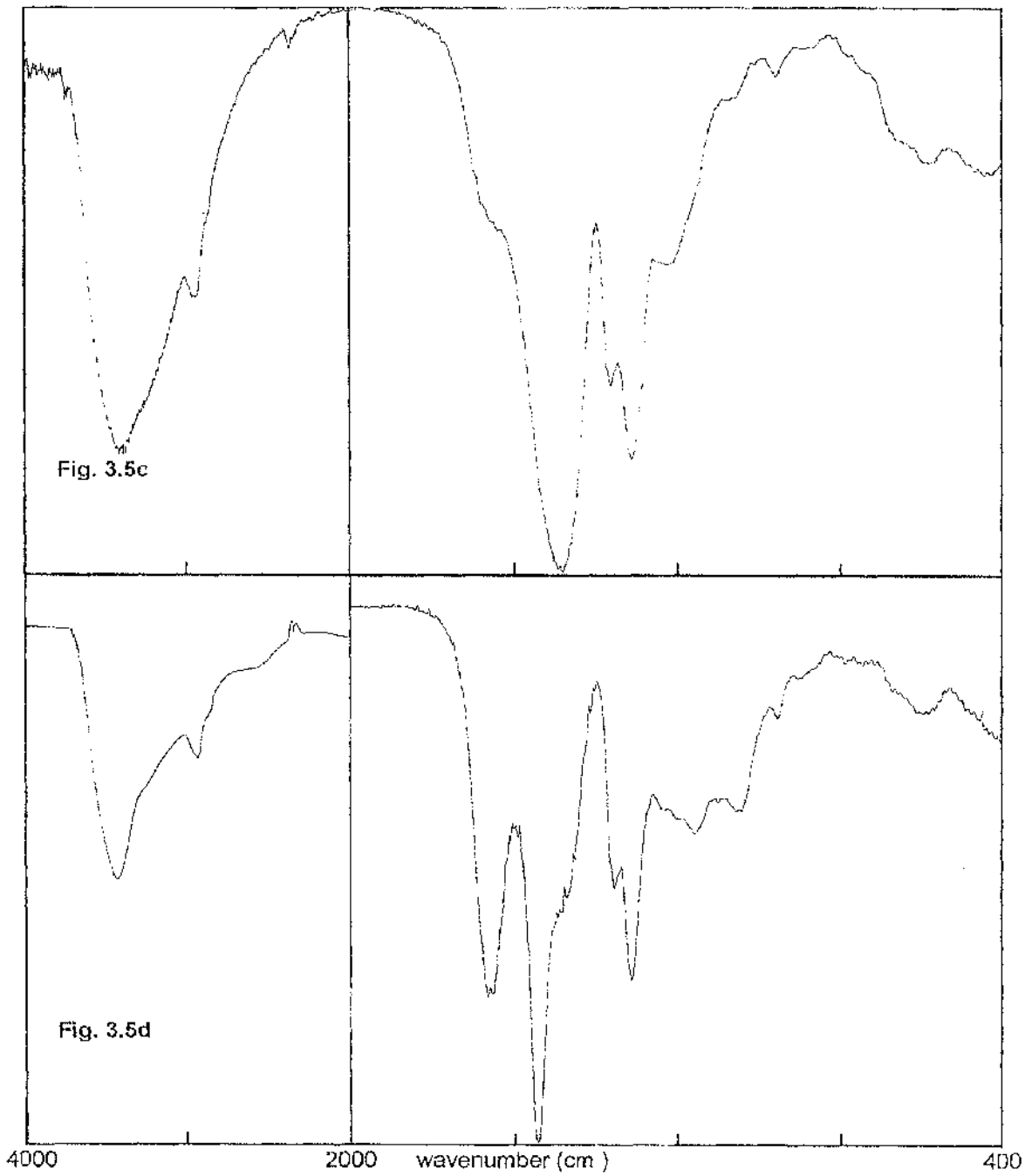


Fig. 3.5c Infra-red spectrum of nickel polyacrylate*.

Fig. 3.5d Infra-red spectrum of copper polyacrylate*.

* made by neutralisation of poly(acrylic acid)

3.6 *PREPARATION OF COPOLYMERS OF STYRENE WITH ACRYLIC ACID*

In this section the methods involved in the preparation of copolymers of styrene with acrylic acid and the subsequent preparation of zinc salts of these copolymers are described.

As the aromatic ring in the styrene molecule can act as both an electron donating or withdrawing centre, styrene can be polymerised by free radical, anionic, cationic or coordination polymerisation. Acrylic acid is polymerised by a free radical mechanism initiated either by photochemical or by thermal decomposition of initiators. Acrylic acid can undergo a controlled polymerisation in solutions of less than 20-30% concentration. The high heat of polymerisation and a large increase in viscosity when polymerised makes the polymerisation difficult to control at high concentrations.

The copolymerisation of styrene with acrylic acid has been carried out in bulk, in solution and as an emulsion.[21] The emulsion polymerisation of styrene with acrylic acid has been studied by a number of workers to produce reduced or soap free polystyrene latexes.[22,23]

The reactivity ratios calculated for the two monomers is dependent on the pH of the reaction mixture. Dissociation of the acrylic acid groups in solution polymerisation reduces their reactivity because of resulting ionic repulsive forces.

3.6.1 Content of Copolymers

Three copolymers were prepared each one having a different proportion of acrylic acid units. The desired percentage of acrylic acid in these

copolymers was 2%, 5% and 10% respectively. The mole fraction of each monomer required in the copolymer feed to achieve these ratios was calculated by the use of the copolymer equation.

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1 + 2 f_1 f_2 + r_2 f_2)$$

where the reactivity ratios have been calculated by *Chapin et al*[24] for copolymerisation in bulk using a radical initiator and recalculated by *Greenley*[25] as

styrene, $r_1 = 0.253$
acrylic acid, $r_2 = 0.136$
f_1=mole fraction of styrene in monomer feed.
f_2=mole fraction of acrylic acid in monomer feed.
F_1= mole fraction of acrylic acid in polymer.
F_2=mole fraction of styrene in polymer.

The mole fractions of acrylic acid and styrene required in the monomer feed for each copolymer calculated from the copolymer equation are given in **Table 3.6.**

3.7 PREPARATION OF COPOLYMERS

3.7.1 Materials

Acrylic acid (Hopkin and Williams Ltd); Styrene (Aldrich); zinc chloride and ammonia (BDH Ltd).

3.7.2 Purification of Starting Materials

Acrylic acid and azobisisobutyronitrile were purified by the methods described in sections 3.3 and 3.4.

Styrene was supplied inhibited with 10-15ppm tert-butylcatechol. Due to the volatility of the inhibitor it cannot be completely removed by distillation of the monomer. The inhibitor was removed prior to distillation by first washing 150ml portions of styrene, three times with a 0.1M aqueous solution of sodium hydroxide and then a further three times with distilled water. It was then dried for 24 hours over anhydrous magnesium sulphate and overnight with calcium hydride.

The styrene was then purified by distillation under reduced pressure, using a water pressure suction pump, at 60°C with the middle fraction being collected and stored in a deep freeze prior to use.

3.8 POLYMERISATION PROCEDURE

The copolymerisations were carried out in bulk at 60°C under vacuum in the same type of sealed tubes as described in section 3.4. The amounts of styrene, acrylic acid and azobisisobutyronitrile used in each polymerisation are given in **Table 3.7**. They were weighed out on a top pan electronic balance and were in turn added to the dilatometer by way of a long-necked filter funnel. The resulting solution was then degassed on a vacuum line by repeated freezing and thawing until the pressure in the vessel had been reduced to 10^{-3} torr, after which the dilatometer was sealed.

The polymerisations were carried out in the constant temperature bath, as described in section 3.4.2 with the extent of reaction being followed by the volume contraction of the reaction mixture. The contraction calculation was based on the assumption that 100% polymerisation of styrene at 60°C is equivalent to a contraction of 17.58%.[26] The polymerisation was halted before a conversion of 5% had occurred, to minimise the effect of composition drift in the monomer feed, by pouring the reaction mixture into a tenfold excess of cold bulk methanol. This resulted in the precipitation of the copolymer which was filtered out of the reaction mixture.

The copolymer was purified by three times dissolving it in dichloromethane (AR Grade) and precipitating the copolymer from the resulting solution in a large excess of methanol (AR Grade).

The reaction conditions and yields for each of the polymerisations are given in **Table 3.8**.

3.9 CHARACTERISATION OF COPOLYMERS

Characterisation of the copolymers was undertaken by microanalysis for carbon and hydrogen content, studying their infra-red spectra and determining their molecular weight by gel permeation chromatography.

3.9.1 Carbon and Hydrogen Content

The carbon and hydrogen content for each copolymer was found by microanalysis, with the use of a Carlo Ebra Elemental Analyser Model no. 1106. The results are given in **Table 3.6**.

From the microanalysis results the empirical formula of the copolymers and the percentage of acrylic acid repeat units in each copolymer have been calculated. It was assumed that the copolymers are both solvent and

moisture free and that the remaining mass is due to oxygen. The amount of initiator fragments in the copolymers have not been used in the calculation, but from molecular weight determination (section 3.9.2) they are less than 0.05% of the total weight.

Polymer	% Carbon		% Hydrogen		% acrylic acid
	Theory	Found	Theory	Found	in copolymer
2% AA/St	91.73	91.70	7.65	7.79	1.7
5% AA/St	90.83	90.72	7.61	7.44	5.8
10% AA/St	89.29	88.19	7.53	8.06	11.8

Table 3.6 Microanalysis results of copolymers

3.9.1a 2% acrylic acid/styrene copolymer

Elemental microanalysis of the copolymer gave the following results C=91.70%, H=7.79% and O=0.51%. This gives an empirical molecular formula of $C_{240}H_{244}O$ which is equivalent to an acrylic acid content of 1.7%.

3.9.1b 5% acrylic acid/styrene copolymer

Elemental microanalysis of the copolymer gave the following results C=90.72%, H=7.44% and O=1.84%. This gives an empirical molecular formula of $C_{66}H_{65}O$ which is equivalent to an acrylic acid content of 5.8%.

3.9.1c 10% acrylic acid/styrene copolymer

Elemental microanalysis of the copolymer gave the following results C=88.19%, H=8.06% and O=3.75%. This gives an empirical molecular formula of $C_{31}H_{34}O$ which is equivalent to an acrylic acid content of 11.8%.

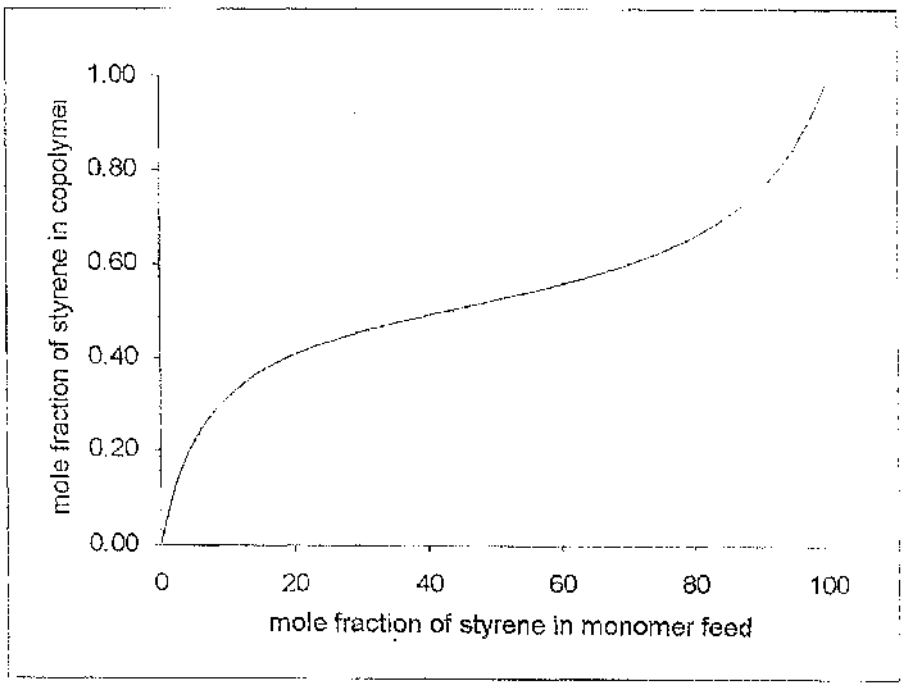


Fig. 3.6 Instantaneous composition of styrene in acrylic acid/ styrene copolymer as function of monomer feed.

The copolymer equation curve of feed composition versus instantaneous copolymer composition calculated using the reactivity ratios for the styrene acrylic acid copolymerisation (**Fig. 3.6**) illustrates that any small error in weighing out sample or the loss of any sample during transfer to the polymerisation vessel would result in the small differences found in the composition of the copolymer. The graph also shows that the composition

drift in the monomer feed, even for the low conversion percentages used during the synthesis of the copolymers, will result in a change in the copolymer composition.

Discrepancies between the theoretical and calculated values of copolymer composition may also be due to the presence of solvent or moisture remaining even after prolonged vacuum drying.

3.9.2 Gel Permeation Chromatography

The average molecular weights and molecular weight distribution of the copolymers were estimated using Gel Permeation Chromatography.

The copolymers were studied as solutions in tetrahydrofuran. Sample solutions were prepared by adding 20 mg of each polymer to 10 ml of tetrahydrofuran and leaving overnight to dissolve. A small amount of dichlorobenzene was added as an internal marker before thoroughly mixing the solutions. Immediately prior to chromatography the solutions were filtered through a 0.2 micron polyamide membrane.

The results obtained (**Table 3.9**) are given as equivalents to the polystyrene samples used to calibrate the system. As a result there may be considerable differences between the results obtained and the actual molecular masses of the sample. In GPC the analytes are separated as a function of their apparent physical size in solution termed the hydrodynamic volume. The effect of the variable amounts of polar acrylic acid units on the chain conformations and apparent physical size in solution of each copolymer compared to polystyrene was not known. It would be expected that polar interactions of the carboxylic acid functional groups would occur and affect the hydrodynamic volume. The assumption had to be made that this affect was minimal.

For comparison of results the molecular mass distribution curves for the three copolymers are shown on the same set of axis in **Fig. 3.7**. Due to the polymerisations being out in bulk with identical initiator concentrations and at the same temperature with only a small difference in acrylic acid concentration it would be expected that the curves are similar. The differences in the curves may be due to a decrease in the rate of polymerisation with increasing acrylic acid content causing longer chain lengths or that the acrylic acid content of the copolymers changes the hydrodynamic volume of the copolymers resulting in experimental error in the GPC results.

3.9.3 Infrared Analysis

The infra-red spectra of the polymers were recorded as thin films on sodium chloride plates. Small amounts of sample were dissolved in dichloromethane and dropped on to a sodium chloride plate. Evaporation of the dichloromethane under a drying lamp yielded a thin film of copolymer deposited on the salt plate. The infrared spectra of the polymers are given in **Fig. 3.8(a)** to **(c)**.

The infra-red bands in the spectrum due to the carboxylic acid groups indicate that many of the carboxylic acid groups exist as hydrogen bonded dimers. At lower temperatures these dimers can act as crosslinks in the polymer if they are intermolecular. The bands at ~1703 cm^{-1} and ~1744 cm^{-1} are due to the carbonyl groups of the acrylic acid units in the copolymer.

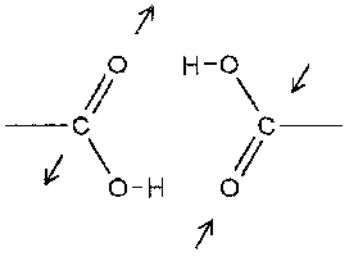


Fig. 3.9 Out of phase $(CO)_2$ stretch.

The band at ~1703 cm^{-1} is a normal mode out of phase $(CO)_2$ stretch (**Fig. 3.9**) for a hydrogen bonded dimer and the band at ~1744 cm^{-1} is the non-hydrogen bonded carbonyl stretch.

The greater intensity of the dimer absorption at ~1703 cm^{-1} compared the non-hydrogen bonded absorption at 1744 cm^{-1} is indicative of the fact that most carboxylic acid groups are in the form of dimers. The spectrum does not reveal whether they are inter- or intramolecular dimers or a combination of both. The weak band at 940 cm^{-1} also is due to the existence of acid dimers and is caused by a normal mode in phase out of plane $(H)_2$ deformation for carboxylic acid dimers (**Fig. 3.10**). The hydrogen bonded O-H stretching band is a broad band with a maximum at ~2650 $cm.^{-1}$

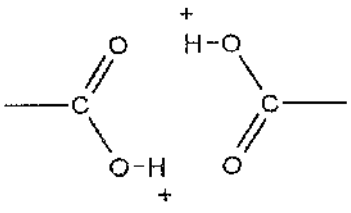


Fig. 3.10 In phase out of plane $(H)_2$ deformation.

Nyquist[27] showed that as the temperature of acrylic acid/styrene copolymers is increased the number of non-hydrogen bonded carboxylic acid groups decreases.

The bands at 1601cm,$^{-1}$ 1583cm^{-1} and 1490cm^{-1} are the C-H stretching modes of the aromatic ring.

3.10 REACTION OF COPOLYMERS WITH ZINC^{2+} IONS

The attempted reaction of the copolymers directly with various zinc compounds proved unsuccessful. It was therefore necessary to prepare these salts through an ammonium salt intermediate which is a well established process for crosslinking carboxylic acid groups with zinc.

3.10.1 Preparation of Zinc Salts of Acrylic acid/ Styrene Copolymers

To a well stirred solution of the copolymer in tetrahydrofuran was added a few drops of concentrated aqueous ammonia solution. The resulting mixture was then stirred for one hour. To this was then added a stoichoimetric excess of zinc chloride with the reaction mixture being stirred for a further hour. The copolymer was precipitated in methanol, washed a further three times with methanol, after which it was dried in a vacuum oven at 40°C for 24 hours.

The polymers were examined by recording their infrared spectra as potassium bromide disks. The spectra of the copolymers are given in **Figs. 3.11(a)** to **(c)**.

The infra-red spectra confirm that the crosslinking reaction has taken place, but that not all acid groups have reacted with a metal ion. The

strong absorption at 1703 cm^{-1} due to the out of phase $(CO)_2$ stretch in acrylic acid dimers found in the acid copolymers is greatly reduced in intensity in the zinc salts and is now weaker than the non-hydrogen bonded carbonyl absorption at 1744 cm^{-1}. The broad O-H stretching band with the maximum at 2650 cm^{-1} has also disappeared. The absorptions due to the carboxylate symmetric and anti-symmetric stretches at 1550-1650 cm^{-1} and ~1430 cm^{-1} are partially obscured by other absorptions of the copolymer.

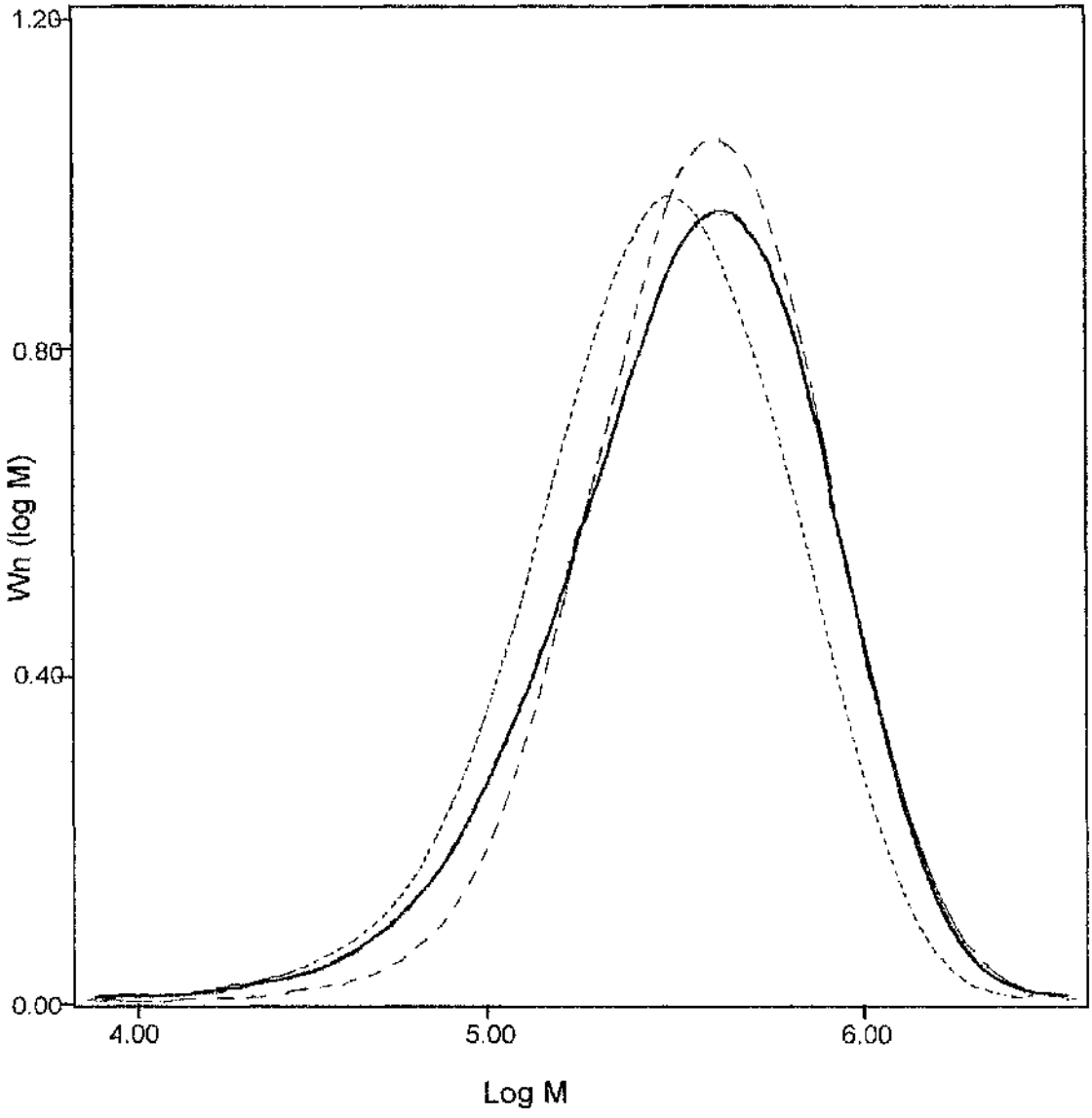


Fig. 3.7 Molecular mass distribution curves obtained for the styrene/acrylic acid copolymers

- - - - Copolymer containing 1.7% acrylic acid units.

— — Copolymer containing 5.8% acrylic acid units.

——— Copolymer containing 11.8% acrylic acid units.

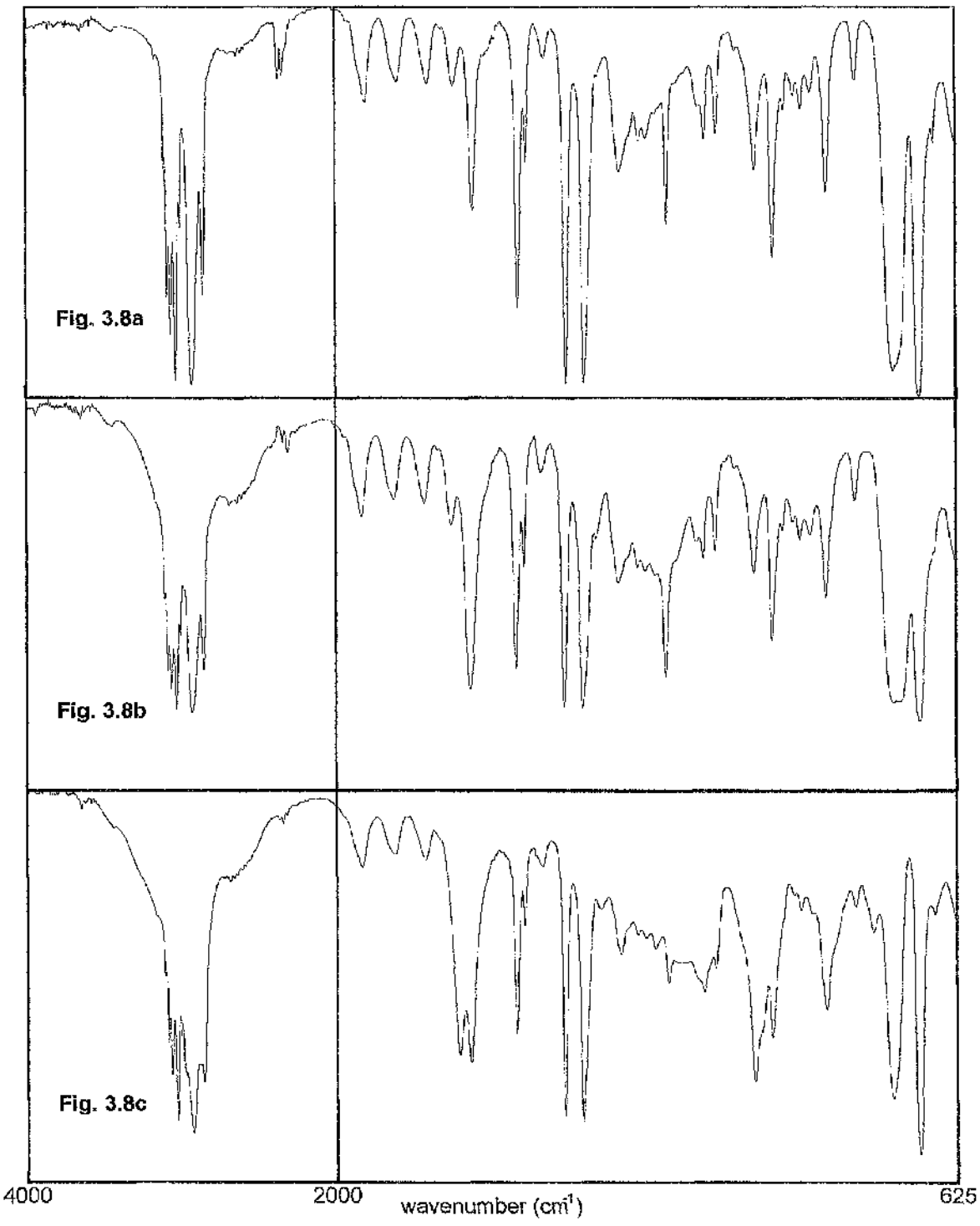


Fig. 3.8a Infra-red spectrum of the styrene/acrylic acid copolymer, containing 1.7% acrylic acid units.

Fig. 3.8b Infra-red spectum of the styrene/acrylic acid copolymer, containing 5.8% acrylic acid units.

Fig. 3.8c Infra-red spectrum of the styrene/acrylic acid copolymer, containing 11.8% acrylic acid units.

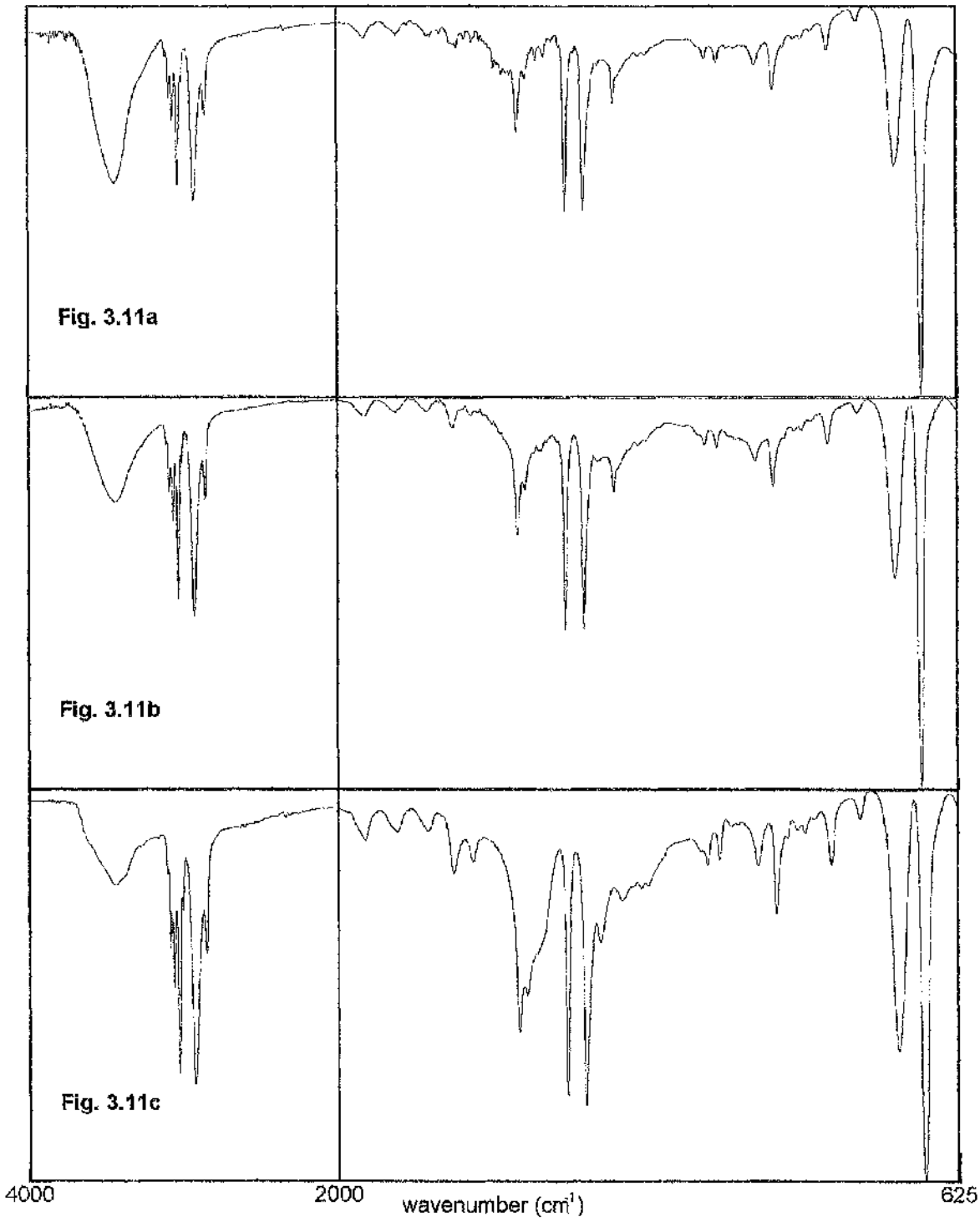


Fig. 3.11a Infra-red spectrum of the zinc salt of the styrene/acrylic acid copolymer, containing 1.7% acrylic acid units.

Fig. 3.11b Infra-red spectum of the zinc salt of the styrene/acrylic acid copolymer, containing 5.8% acrylic acid units.

Fig. 3.11c Infra-red spectrum of the zinc salt of the styrene/acrylic acid copolymer, containing 11.8% acrylic acid units.

	f_1	f_2	F_1	F_2
2% acrylic acid	0.995	0.005	0.980	0.020
5% acrylic acid	0.986	0.014	0.952	0.048
10% acrylic acid	0.970	0.030	0.909	0.091

Table 3.7 Mole fraction of monomer in copolymer feed.

% Acrylic Acid in Copolymer	Weight of Styrene (g)	Weight of Acrylic Acid (g)	Initiator (w/v%)	Time (hours)	Conversion (%)
1.7	38.93	0.18	0.01	8	4.3
5.8	81.12	0.80	0.01	5	4.0
11.8	79.58	1.54	0.01	5	3.1

Table 3.8 Copolymerisation Data for Styrene / Acrylic Acid Copolymers.

	M_w	M_n	Polydispersity
1.7% acrylic acid/	429,000	192,000	2.2
styrene	425,000	192,000	2.2
5.8% acrylic acid/	567,000	286,000	2.0
styrene	581,000	301,000	1.9
11.8% acrylic acid/	543,000	228,000	2.4
styrene	545,000	238,000	2.3

Table 3.9 GPC results for styrene/acrylic acid copolymers.

CHAPTER FOUR

THERMAL DEGRADATION OF TRANSITION METAL SALT POLYACRYLATES

4.1 INTRODUCTION

Two of the most common and important monomer units present in ionic polymers are the salts of acrylic and methacrylic acids.

In this chapter the thermal stability and degradation of transition metal salt homopolymers, of the first series, of poly(acrylic acid) are studied. The metals used in this study were cobalt, nickel, copper and zinc. The methods used to prepare the polymers are described in chapter two. Possible degradation reaction mechanisms are discussed with respect to the products of degradation.

The majority of studies carried out on the thermal stability and degradation properties of polymers with structures based on acrylic and methacrylic acids have involved the esters of these acids[28-33], with less work having been carried out on their metal salts.

Most of the previous studies on the metal salts of the acids have involved polymers and copolymers of alkali and alkaline earth metal salts[34-41] with less work done on salts of transition metals. An increase in interest in recent years in this group of metals has occurred, due to their suggested use as co-ordinating or conducting polymers.

Although less commonly used than first and second group metal salts of acrylic acid, the transition metal salts have been utilised both as

homopolymers and in copolymers for various applications, usually for improved toughness or adhesion.

Of the metals, the most widely used monomer is zinc acrylate which has found use as a crosslinking agent for improved strength of butadiene in golf ball cores[42] and in floor tiles[14]. It has been added to low stress soldering, heat resistant epoxy resin compositions for sealing electronic devices to improve cracking failure resistance.[43] Zinc polyacrylate gels are commonly used as a dental cements because of their adhesive properties and rapid rate of setting.[10] Zinc acrylate has also been added to butadiene-methyl methacrylate copolymers to produce rubber vibration dampers with improved adhesion to metals.[44]

Copper acrylate has been copolymerised with barium and yttrium acrylates to form a copolymer used as a precursor in the synthesis of $YBa_2Cu_3O_x$ semiconductors.[45]

The thermal behaviour of poly(acrylic acid) has been studied by many workers.[46-50] In this laboratory the thermal degradation of poly(acrylic acid) was studied under TVA conditions by Sadeghi.[49]

The first stage of degradation involves dehydration by intramolecular cyclisation of adjacent monomer units to give six member anhydride ring structures. Decarboxylation becomes important at 250°C with water and carbon dioxide being evolved up to 500°C. A number of other volatile products including trace amounts of monomer are evolved.

Eisenberg[47] showed that the type of anhydride structure formed is dependent on the temperature. He found that intermolecular ring formation is favoured above 200°C, with intramolecular rings predominating at lower temperatures of about 150°C.

It has been established that metal salts of simple carboxylic acids will undergo thermal decarboxylation, it is thought mainly via a free radical mechanism, resulting in the metal oxide and ketones as major degradation products.[51-53]

Nicholson[54-56] studied the thermal behaviour of partially neutralised poly(acrylic acid) at 250°C. He concluded that the occurrence of dehydration and subsequent decarboxylation is dependent on the ionic nature of the counter ion involved, as well as its valency. Univalent cations appear to assist in anhydride decarboxylation to form crosslinked ketonic structures, while decarboxylation does not occur with multivalent cations.

The thermal degradation mechanisms of fully neutralised poly(acrylic acid) metal salts differ from those of the acid or partially neutralised acid, because of the inability of these polymers to form acid anhydride structures by dehydration of pairs of carboxylic acid groups.

A number of studies have been carried out on the thermal degradation of alkali and alkaline earth metal salts of poly(methacrylic acid) and poly(acrylic acid).

McNeill and Zulfiqar proposed alkali[37] and alkaline earth[38] metal polymethacrylates decompose by a radical mechanism, via side and main chain scission of the polymer.

The products of degradation consisted of monomer, metal isobutyrate, metal oxide or carbonate, hydrogen, carbon monoxide, carbon dioxide, aliphatic ketones and saturated and unsaturated hydrocarbons.

Monomer and isobutyrate found in the alkali metal polymethacrylates, do not occur to the same extent in the corresponding alkaline earth polymethacrylates, with the exception of magnesium, because of the inability of the monomers and isobutyrates to distil out of the degradation zone.

In the corresponding polyacrylates similar types of degradation products are obtained with the exception of monomer and isobutyrate. Sadeghi[34,35] found the thermal degradation occurred by side or main chain scission. Appreciable differences in the relative amounts of volatile products were seen, due to the stronger ionic bonding in the alkaline earth metals,.

Gronowski and Wojtczak[57] studied the thermal stability and kinetics of decomposition of cobalt, nickel, copper and zinc acrylates and the corresponding polymers by thermogravimetry and differential thermal analysis. They found that their thermal stability followed the sequence, Zn>Co>Ni>Cu and correlated an increase in the activation energy of decomposition of the polymers with an increased cross-linking density.

Dzhardimalieva[58] found that the cobalt, nickel and copper polyacrylates had predominately syndiotactic structures and were thermally stable, with degradation temperatures to 400°C.

McNeill and Zulfiqar[59,60] studied the thermal degradation of the zinc, cobalt, nickel and copper salts of poly(methacrylic acid). They found the zinc, cobalt and nickel polymethacrylates to be much more stable than copper polymethacrylate, although the degradation products were similar.

The techniques used to study the degradation of these polymers were Differential Thermal Analysis (DTA), Thermogravimetry (TG) and Thermal Volatilisation Analysis (TVA). The polymers were all studied as powders

because their insolubility in any solvent and their inability to melt, due to their ionic nature, made the casting of films impossible.

In the subsequent sections of this chapter the polymers made by neutralisation of poly(acrylic acid) will be marked with the symbol (*) to distinguish them from the polymers made by polymerisation of the metal acrylate monomers.

4.2 THERMOGRAVIMETRIC ANALYSIS

In thermogravimetric analysis samples of approximately 5 mg, in the form of finely ground powders, were heated under a nitrogen flow of 50 ml/min, to 500°C, at 10°C/min.

The TG results obtained for the polymers are shown in **Figs. 4.1** to **4.4**. The decomposition data for the nickel, cobalt and zinc polyacrylates is given in **Table 4.1** and for the copper polyacrylates in **Table 4.2**. For comparison the results obtained for each metal, prepared by the two different methods, are illustrated on the same graph.

All the polymers show a gradual weight loss preceding the main degradation step. The early weight loss, up to approximately 200°C, can be attributed to the removal of methanol or water, the solvents remaining from the preparative stage, or moisture absorbed from the atmosphere during storage. Due to the highly ionic, crosslinked nature of these polymers removal of the solvents required prolonged heating at elevated temperatures of 80-100°C.

Also responsible for the weight loss at this stage is the co-ordinated water found in the cobalt and nickel monomers. Dzhardimalieva[58] found the co-ordination of the metals did not change during polymerisation so that any

complexed water present in the monomer would remain in the polymer. The weight loss for this stage is less for the zinc and copper polymers, which did not contain water in the monomers, than for the cobalt and nickel polymers which did.

The polymers made by neutralisation all showed a greater weight loss up to main degradation step than the polymers made by polymerisation. This is possibly due to decomposition reactions undergone by the unreacted carboxylic acid groups present in these polymers.

The main decomposition of the polymers occur as a single stage process for the cobalt, nickel and zinc polyacrylates while the degradation of the copper polyacrylates take place over a series of stages.

In the zinc, cobalt and nickel polyacrylates, the temperature of maximum rate of weight loss, for each metal, is similar for the polymers made by polymerisation and neutralisation, differing by a maximum of 6°C.

After the main degradation step all of the polymers continue to show a gradual weight loss up to and beyond 500°C.

At 500°C any metal carbonate that may have formed would have in all cases decomposed. The residual weight of the polymers after the main degradation step is greater than the theoretical value obtained if the polymers were reduced completely to the metal or metal oxide, suggesting the presence of some form of carbonaceous residue.

In all four cases the polymers made by neutralisation showed a greater total weight loss to 500°C than the equivalent polymer made by polymerisation. This may be due to the polymers made by neutralisation

having a lesser metal content and therefore a greater proportion of degradable hydrocarbon material.

The TG curves for zinc polyacrylate and zinc polyacrylate* (**Fig. 4.1**) show initial weight losses of 5.2% and 7.5%, up to 200°C. Between 200°C and 325°C, the onset temperature for the main degradation step, there is a gradual weight loss accounting for 3.1% and 2.3% of the total weight, respectively. The main degradation step takes place between 350°C and 500°C, where weight losses of 35.2% and 40.5% occur. The maxima in the DTG curves occur at 451°C for zinc polyacrylate and 449°C for zinc polyacrylate*. The total weight loss to 500°C is therefore 43.5% for zinc polyacrylate and 50.3% for zinc polyacrylate*.

For cobalt polyacrylate and cobalt polyacrylate* (**Fig. 4.2**) the weight losses up to 200°C are 6.7% and 11.7%. Between 200°C and 350°C the weight losses are 3.2% and 10.2%. The maximum rate of weight loss occurs at 447°C for cobalt polyacrylate and 445°C for cobalt polyacrylate*. The weight losses for this stage are 42.1% and 38.9% respectively. At 500°C 52.1% of the original weight is lost in cobalt polyacrylate and 60.8% in cobalt polyacrylate*.

For nickel polyacrylate and nickel polyacrylate* (**Fig. 4.3**) the weight losses up to 200°C are 8.7% and 10.2%. Between 200°C and 290°C the weight losses are 1.7% and 2.5%. The maximum rate of weight loss occurs at 385°C for nickel polyacrylate and 391°C for nickel polyacrylate*. The weight losses for this stage are 45.0% and 46.8% respectively. At 500°C 55.4% of the original weight is lost in nickel polyacrylate and 59.5% in nickel polyacrylate*.

The temperature range of the main degradation step of the nickel polymers, was greater than that for the cobalt and zinc polymers. From

DTG, nickel polyacrylate degraded over a temperature range of 140°C and nickel polyacrylate* over 110°C. The broadening of this band could be due to the formation and subsequent degradation of nickel carbonate. The degradation temperature of nickel carbonate at 402°C is higher than for cobalt and zinc. The latter two carbonates if formed in the main degradation step, would immediately decompose to the metal oxide and carbon dioxide, unlike nickel carbonate which would be stable at the degradation temperature of the nickel polyacrylates and subsequently degrade to nickel oxide and carbon dioxide.

The initial weight loss for copper polyacrylate (**Fig. 4.4**) is the smallest of all the samples studied at only 3.5% up to 150°C with an 8.0% weight loss found for copper polyacrylate.*

The decomposition of copper polyacrylate occurs in three stages with peaks in the rate of weight loss at 222°C, 247°C and 262°C. The largest weight loss for any single stage of degradation is in the range 218°C to 258°C where 20.0% of the total weight is lost. After the final peak at 262°C there is a continuous gradual weight loss to 500°C, amounting to 7.0% of the starting weight. The total weight loss to 500°C was 50.0%.

In copper polyacrylate* there are four stages of degradation with maxima at 230°C, 257°C, 315°C and 420°C. The weight losses for the first two stages are 9.0% and 9.5%. The largest single stage of degradation is between 292°C and 362°C where 18.5% of the starting weight is lost. Between 362°C and 500°C there is a 15.5% weight loss. 60.5% of the total weight of copper polyacrylate* is lost at 500°C.

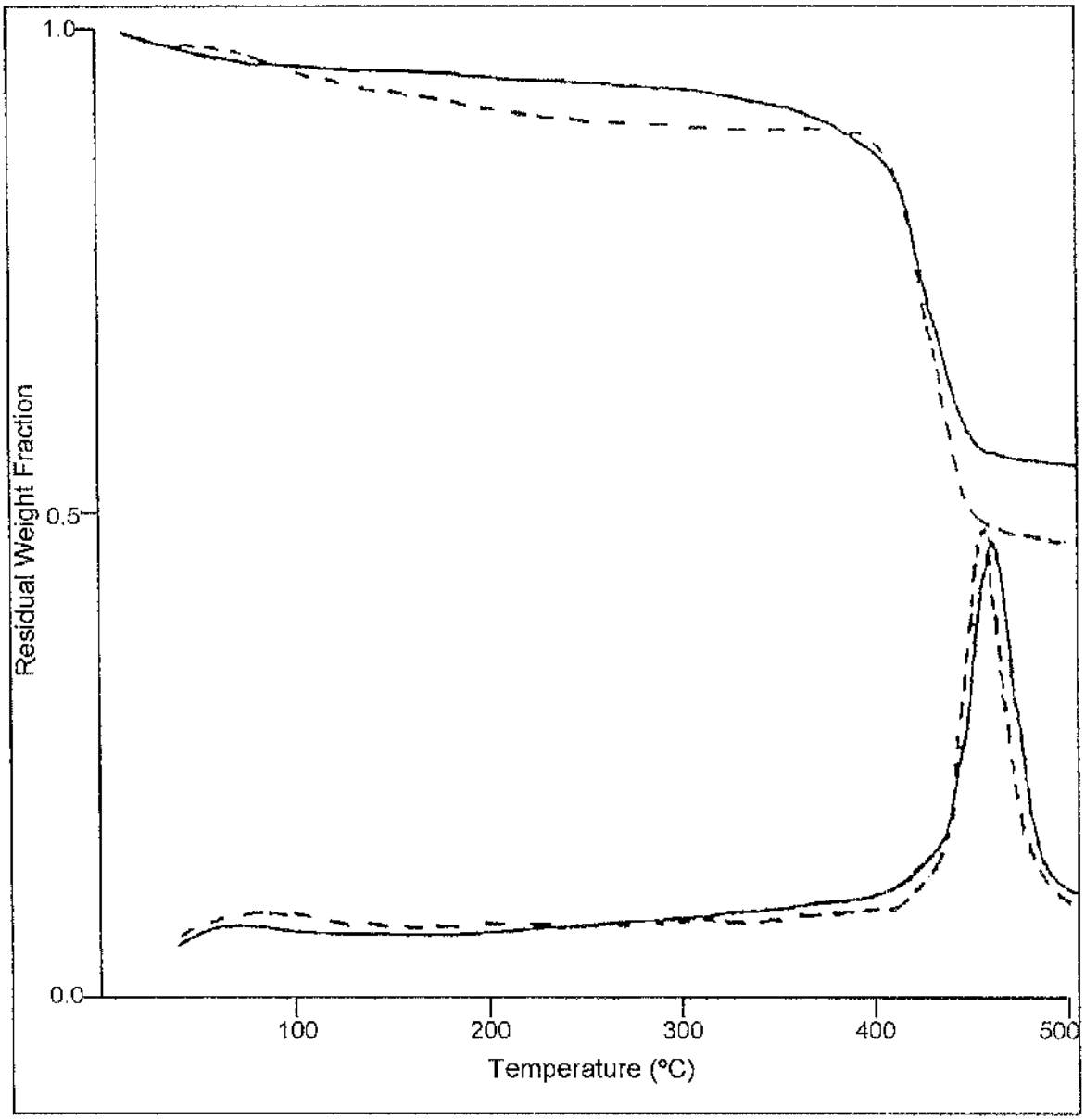


Fig. 4.1 TG and DTG curves (heating rate 10°C/min) of zinc polyacrylate made by polymerisation and neutralisation.

——— Zinc polyacrylate made by polymerisation.

– – – – – Zinc polyacrylate made by neutralisation.

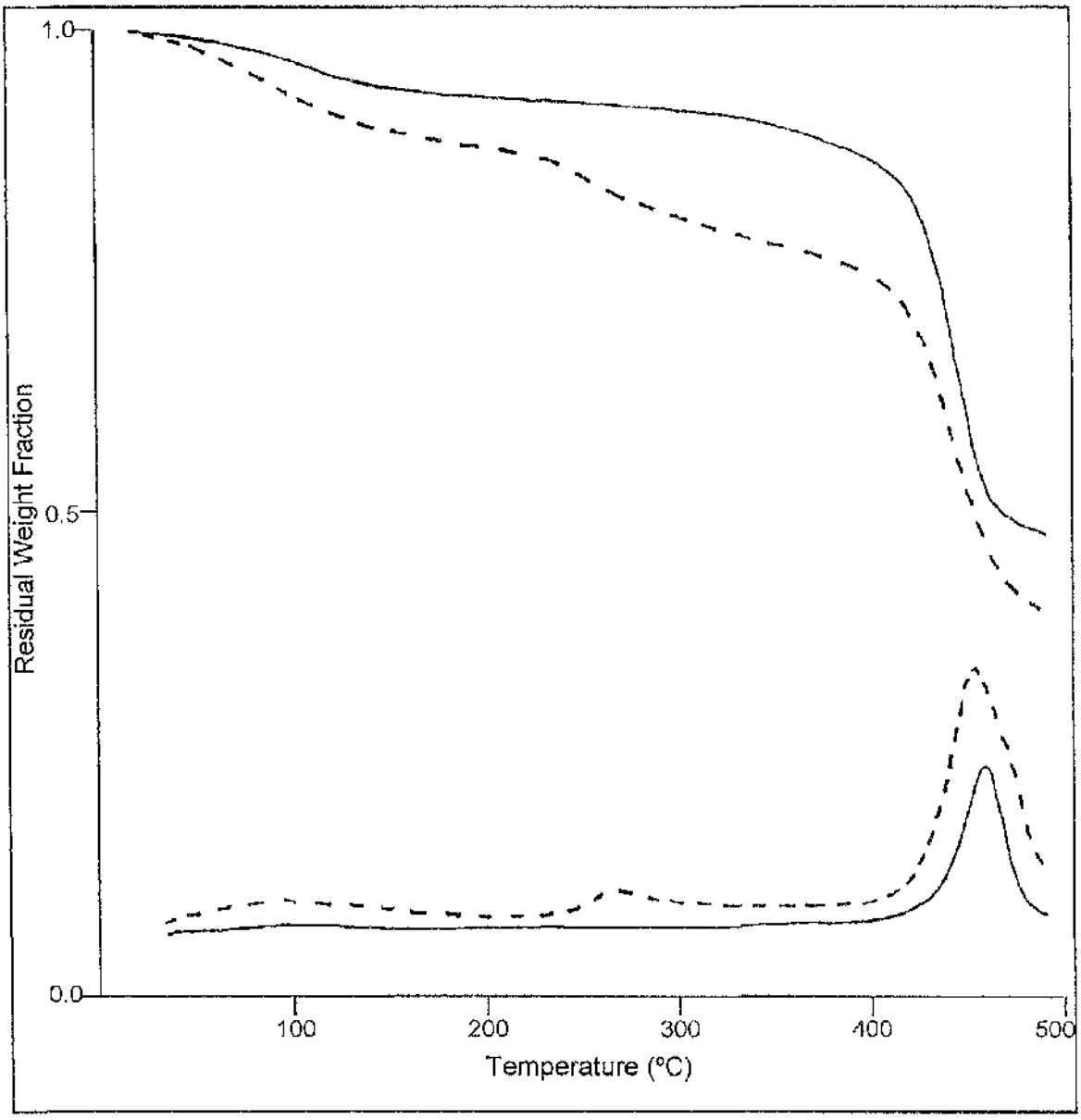


Fig. 4.2 TG and DTG curves (heating rate 10°C/min) of cobalt polyacrylate made by polymerisation and neutralisation.

——— Cobalt polyacrylate made by polymerisation.

- - - - - Cobalt polyacrylate made by neutralisation.

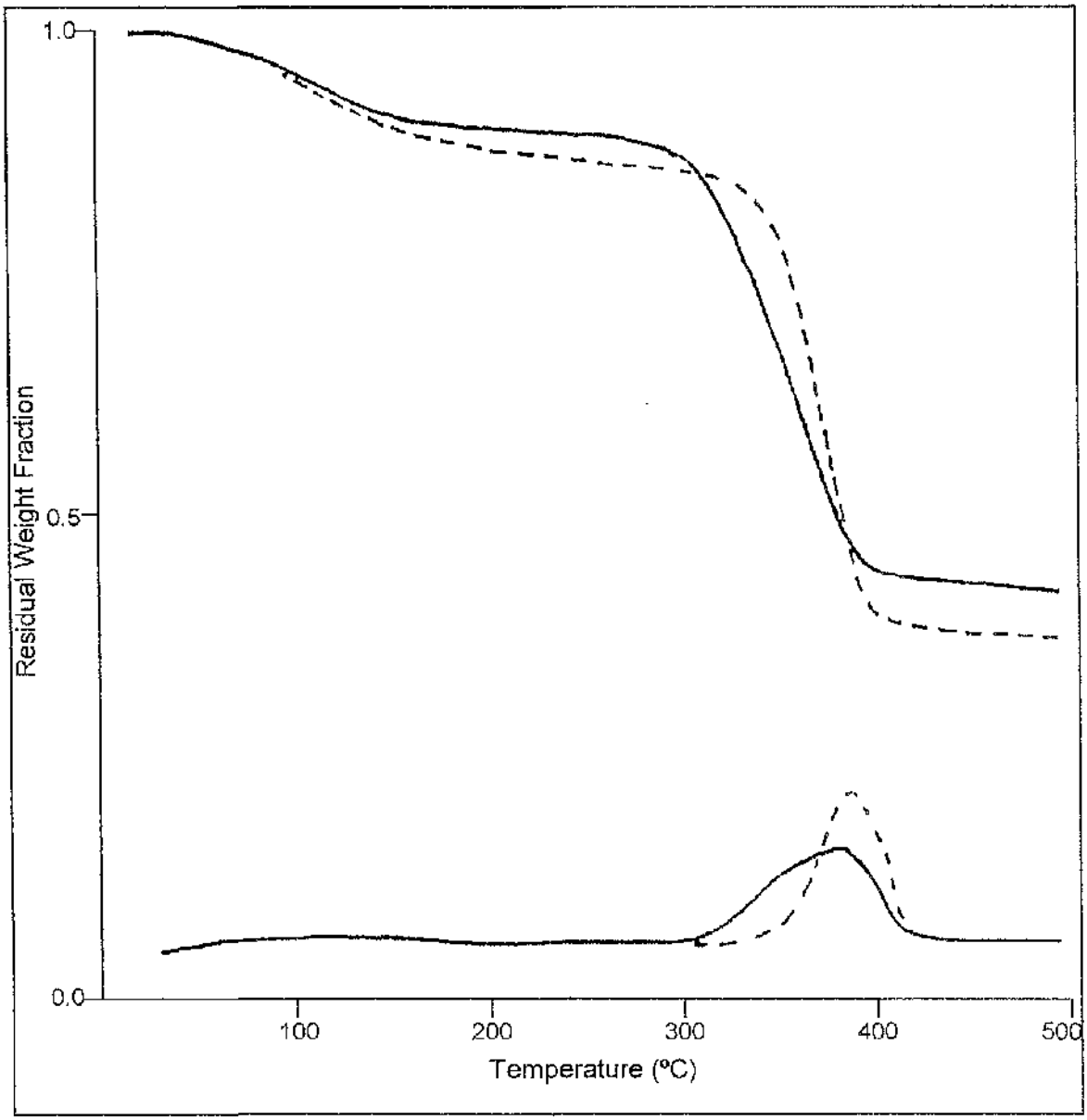


Fig. 4.3 TG and DTG curves (heating rate 10°C/min) of nickel polyacrylate made by polymerisation and neutralisation.

——— Nickel polyacrylate made by polymerisation.

- - - - - Nickel polyacrylate made by neutralisation.

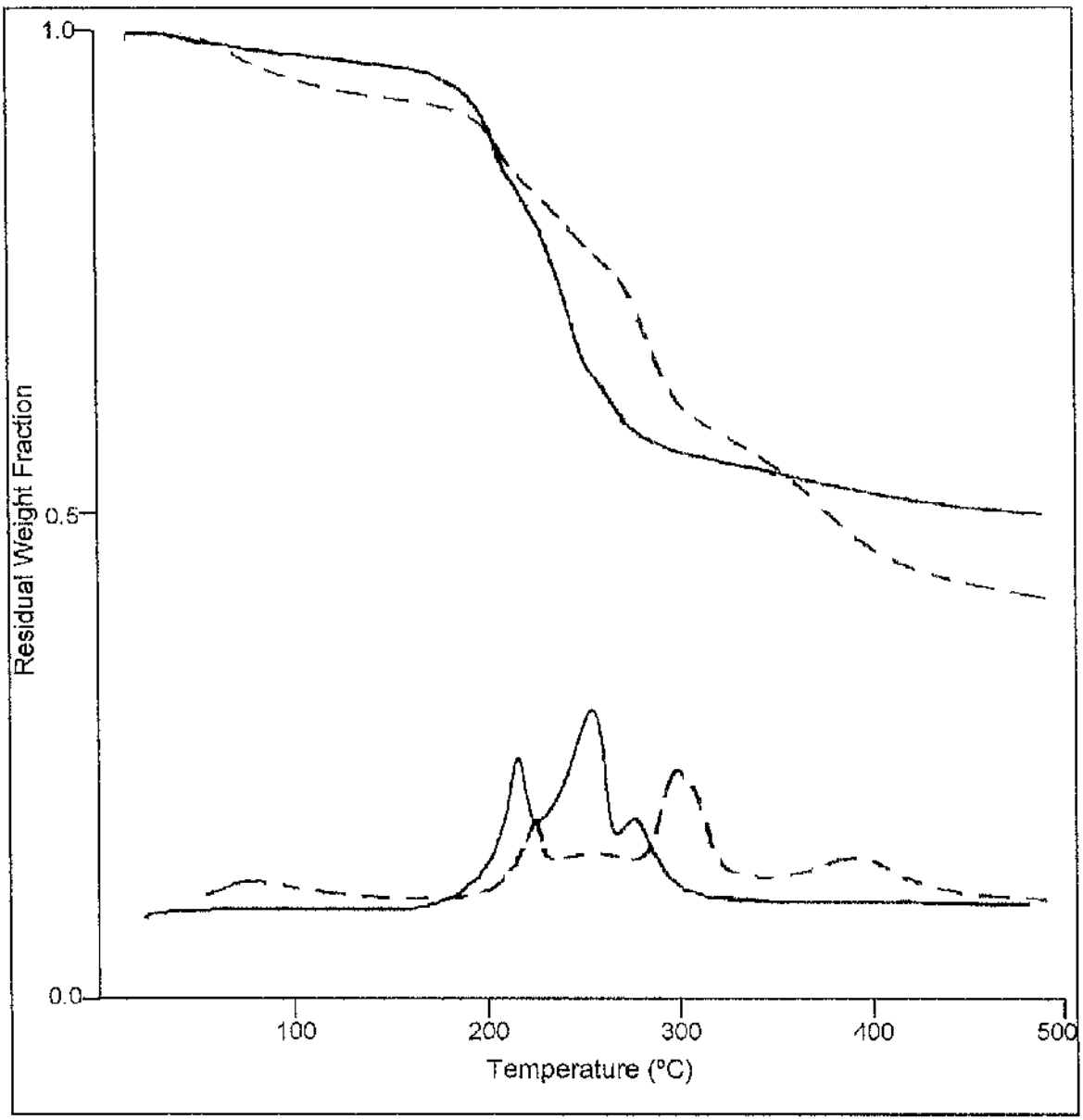


Fig. 4.4 TG and DTG curves (heating rate 10°C/min) of copper polyacrylate made by polymerisation and neutralisation.

——— Copper polyacrylate made by polymerisation.

- - - - - Copper polyacrylate made by neutralisation.

4.3 DIFFERENTIAL THERMAL ANALYSIS

In differential thermal analysis samples in the form of finely ground powders, of approximately 10 mg, were heated under a nitrogen flow of 50 ml/min, up to 500°C, at a rate of 10°C/min.

The results for each of the metal salts, made by polymerisation of the metal acrylates and neutralisation of poly(acrylic acid), are given on the same set of axes in **Figs. 4.5** to **4.8** with the results for the nickel, cobalt and zinc polyacrylates listed in **Table 4.1** and the copper polyacrylates in **Table 4.2**.

The results for the zinc, cobalt and nickel polymers follow a similar pattern. There are two endothermic peaks. The first peak between 100°C and 200°C is due to the release of solvent and/or moisture from the polymers. The second and larger endothermic peak is due to the degradation of the polymers.

In the zinc polyacrylates (**Fig. 4.5**) there is a single endothermic peak at 457°C for zinc polyacrylate and 463°C for zinc polyacrylate*.

In cobalt polyacrylate* (**Fig. 4.6**) there is a minimum at 438°C with a shoulder at 450°C, while the cobalt polymer made by polymerisation has a single peak with a minimum at 450°C.

The main degradation step in both nickel polyacrylates (**Fig. 4.7**) consists of two peaks. The first peak, the larger of the two, has a minimum at 402°C for nickel polyacrylate and 407°C for nickel polyacrylate*, while the second peaks are at 423°C and 425°C respectively.

As was the case in TG analysis, the DTA results for the copper polyacrylates (**Fig. 4.8**) consist of a series peaks, all of them endothermic.

In copper polyacrylate after the endothermic solvent release below 220°C there is a narrow peak at 223°C, a broader one with a shoulder at 247°C and a minimum at 262°C followed by a broad peak between 275°C and 475°C with no well defined minimum.

Copper polyacrylate* has an initial peak at 70°C. A broad peak maximum at 167°C between 90°C and 248°C is followed by a sharp peak with a minimum at 253°C and two broader peaks between 255°C-344°C and 345°C-475°C with minima at 300°C and 447°C respectively.

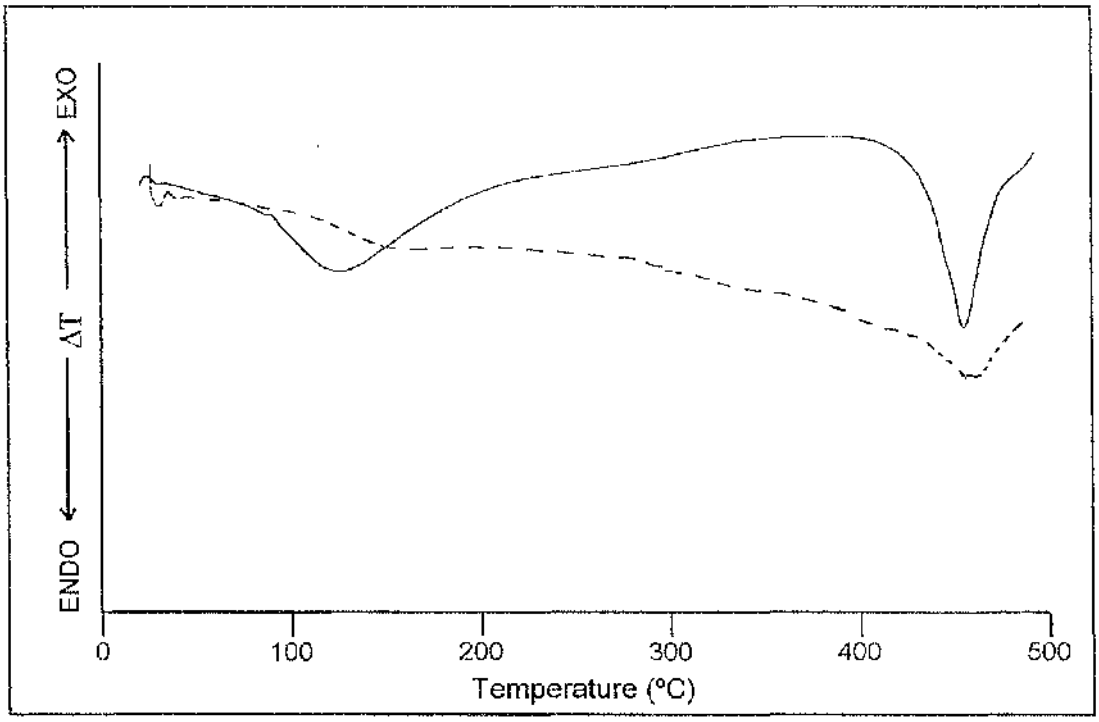


Fig. 4.5 DTA curves (heating rate 10°C/min) of zinc polyacrylate made by polymerisation and neutralisation.

——— Zinc polyacrylate made by polymerisation.

– – – – – Zinc polyacrylate made by neutralisation.

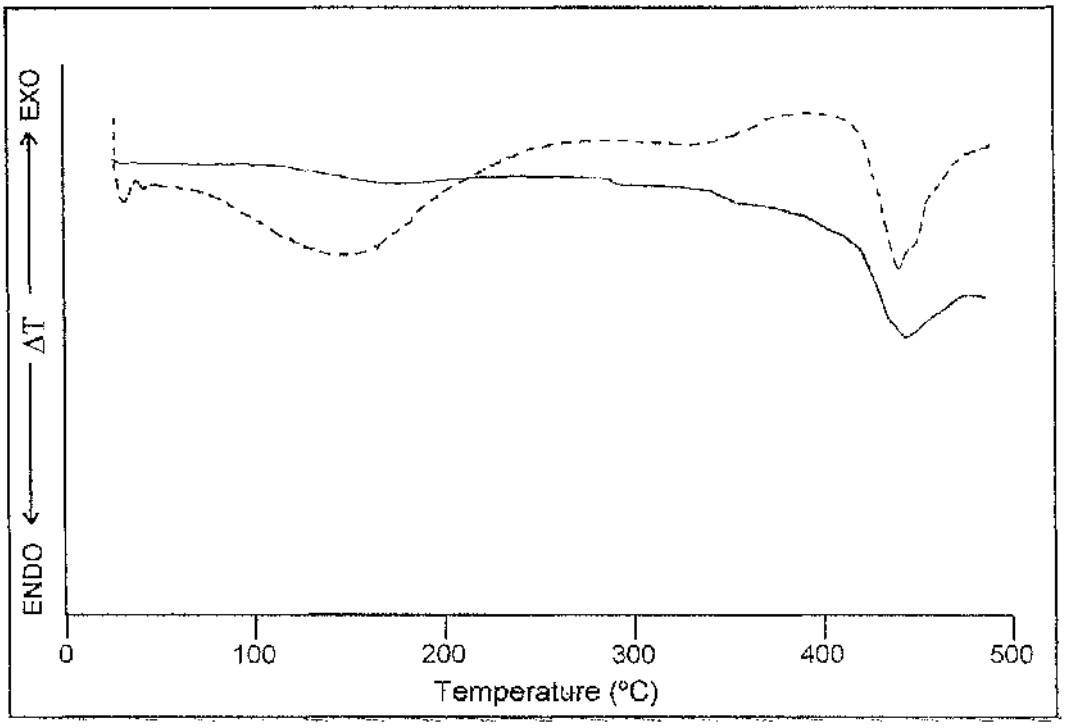


Fig. 4.6 DTA curves (heating rate 10°C/min) of cobalt polyacrylate made by polymerisation and neutralisation.

——— Cobalt polyacrylate made by polymerization.

- - - - - Cobalt polyacrylate made by neutralisation.

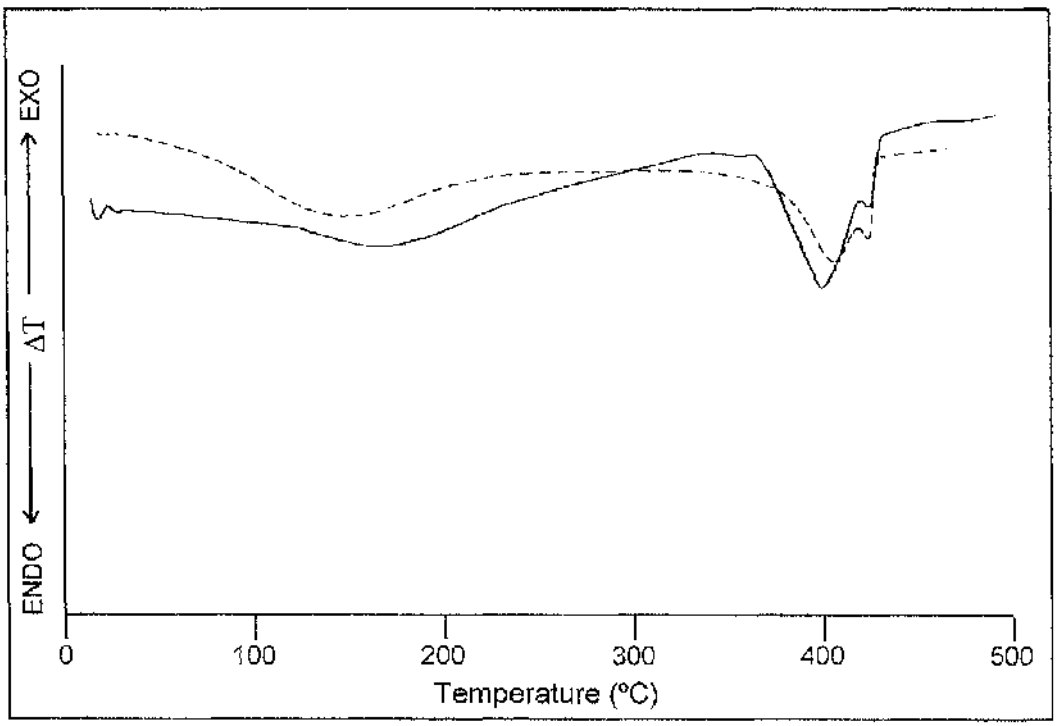


Fig. 4.7 DTA curves (heating rate 10°C/min) of nickel polyacrylate made by polymerisation and neutralisation.

——— Nickel polyacrylate made by polymerization.

– – – – – Nickel polyacrylate made by neutralisation.

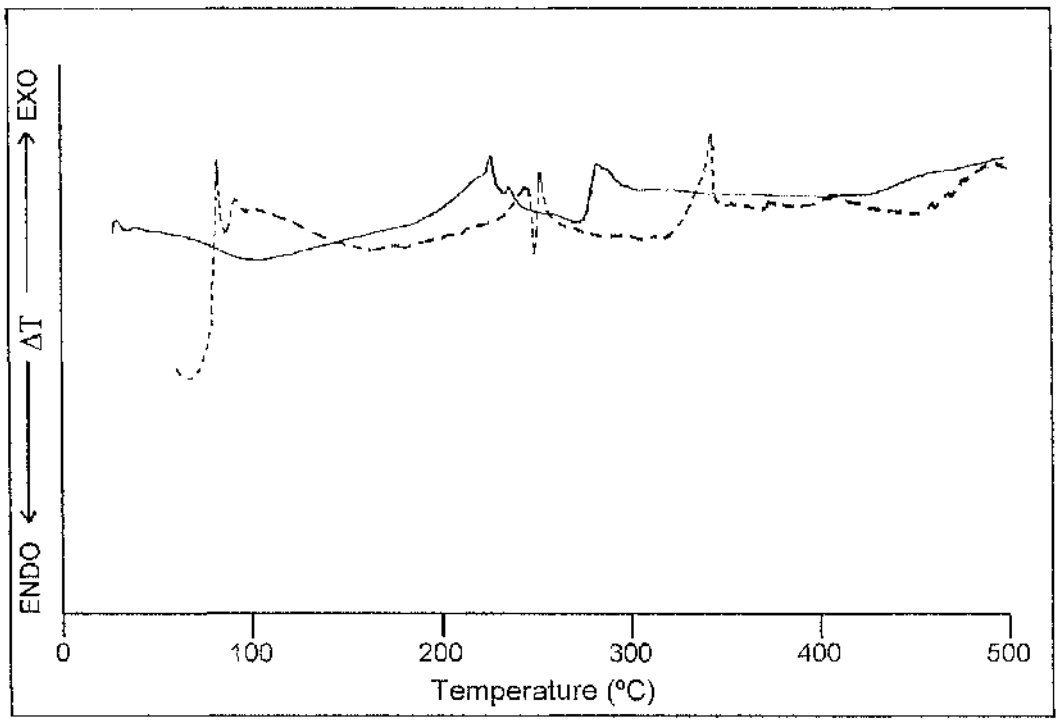


Fig. 4.8 DTA curves (heating rate 10°C/min) of copper polyacrylate made by polymerisation and neutralisation.

——— Copper polyacrylate made by polymerization.

– – – – – Copper polyacrylate made by neutralisation.

	DTG		TG		DTA	
	Peak Temp. °C	Temp. Range °C	% Weight loss for Stage	% Weight loss to 500°C	Peak temp. °C	Temp. range °C
	75°C	>200	5.2			
ZnPA	-	200 -350	3.1	43.5	456	350-485
	451°C	350 -500	35.2			
	85	>200	7.5			
ZnPA*	-	200 -350	2.3	50.3	456	400-480
	449	350 -500	40.5			
	105	>200	6.7			
CoPA	-	200 -350	3.2	52.1	450	400-477
	447	350-500	42.1			
	97	>200	11.7			
CoPA*	-	200-350	10.2	60.8	438	400-445
	445	350-500	38.9		450	445-475
	125	>200	8.7			
NiPA	-	200-295	1.7	55.4	402	367-419
	385	290-500	45.0		423	419-431
	125	>200	10.2			
NiPA*	-	200-315	3.0	59.5	407	350-424
	391	300-500	46.3		425	424-430

Table 4.1 TG, DTG and DTA data for transition metal salt homopolymers of poly(acrylic acid).

* made by neutralisation

	DTG		TG		DTA	
	Peak Temp. °C	Temp. Range °C	% Weight loss for Stage	% Weight loss to 500°C	Peak temp. °C	Temp. range °C
CuPA	-	<150	3.5	50.0	95	>214
	209	155-218	11.5		222	214-225
	247	218-258	20.0		247	225-250
	267	258-300	6.0		262	250-270
	-	>300	7.0		400	270-500
CuPA*	75	<150	8.0	60.5	70	>90
	230	170-243	9.0		167	90-248
	257	243-292	9.5		253	248-255
	315	292-362	18.5		300	255-344
	420	362-500	15.5		447	344-500

Table 4.2 DTG and TG data for copper salts of poly(acrylic acid).

* made by neutralisation

4.4 THERMAL VOLATILISATION ANALYSIS

Thermal Volatilisation Analysis (TVA), described in chapter 2.1, was the third method used to study the thermal degradation of the polyacrylates. The polymers in the form of finely ground powders, with sample weights of approximately 80mg, were heated under vacuum to 500°C at 10°C/min.

The Pirani gauge responses with respect to sample temperature for each of the eight polymers are shown in **Figs. 4.9** to **4.12** with the results listed in **Table 4.3**. The five Pirani gauges were positioned on the vacuum line (**Fig 2.3**) after traps cooled to 0°C, -45°C, -75°C, -100°C and -196°C respectively.

The TVA curves for all the polymers have an initial small peak from ambient temperature to about 200°C, with a maximum at approximately 80°C. This is due to the loss of solvent, moisture or complexed water from the samples. A response is seen on all the Pirani gauges except those after the -100°C and -196°C traps.

The main peak in zinc polyacrylate has an onset temperature of 353°C and a maximum at 470°C. The results obtained for the zinc polymer made by neutralisation of a poly(acrylic acid) are similar. The main evolution of volatiles commences at 348°C, with the maximum at 462°C.

Cobalt polyacrylate has an onset temperature of 346°C and a maximum at 460°C. In cobalt polyacrylate* the onset temperature is 336°C, with the maximum at 456°C. A prominent shoulder is seen on the TVA curve at 410°C.

For nickel polyacrylate the onset temperature is 270°C with the maximum at 402°C. The curve obtained is much broader than for the zinc and cobalt

polymers. The nickel polymer made by neutralisation has a higher onset temperature of 297°C with a maximum at 405°C. It is not as broad a curve as the polymer made by polymerisation.

In the TVA traces of the zinc, cobalt and nickel polyacrylates the 0°C, -45°C, -75°C and -100°C curves are close together while there is a greater separation between them and the -196°C curve. This would suggest that large amounts of highly volatile gaseous products were evolved during degradation. A large amount of non-condensable products, identified in section 4.5.1, were also evolved from the polymers. The larger Pirani gauge responses for the cobalt polymers suggests they produce greater amounts of volatiles than the nickel and zinc polymers.

The copper polymers have more complicated TVA curves. Both consist of three separate peaks, but they occur at different temperatures for each of the polymers.

In copper polyacrylate the onset temperature for the first peak is at 110° C with the maximum at 238°C. The second peak between 256°C and 330°C, has its maximum at 302°C and a shoulder at 260°C. The final broad peak ranging from 330°C to 500°C has a maximum at 405°C. In copper polyacrylate* the first peak is smaller than for the polymer made by polymerisation. The onset temperature is 205°C, with the maximum at 249°C. The second peak, between 260°C and 360°C, has its maximum at 335°C and the third broad peak from 360°C has a maximum at 430°C.

The 0°C, -45°C, -75°C and -100°C curves for the copper polymers are nearly coincident. suggesting that a majority of the degradation products are volatile at -100°C. Non-condensable products are seen in all stages of degradation of both polymers.

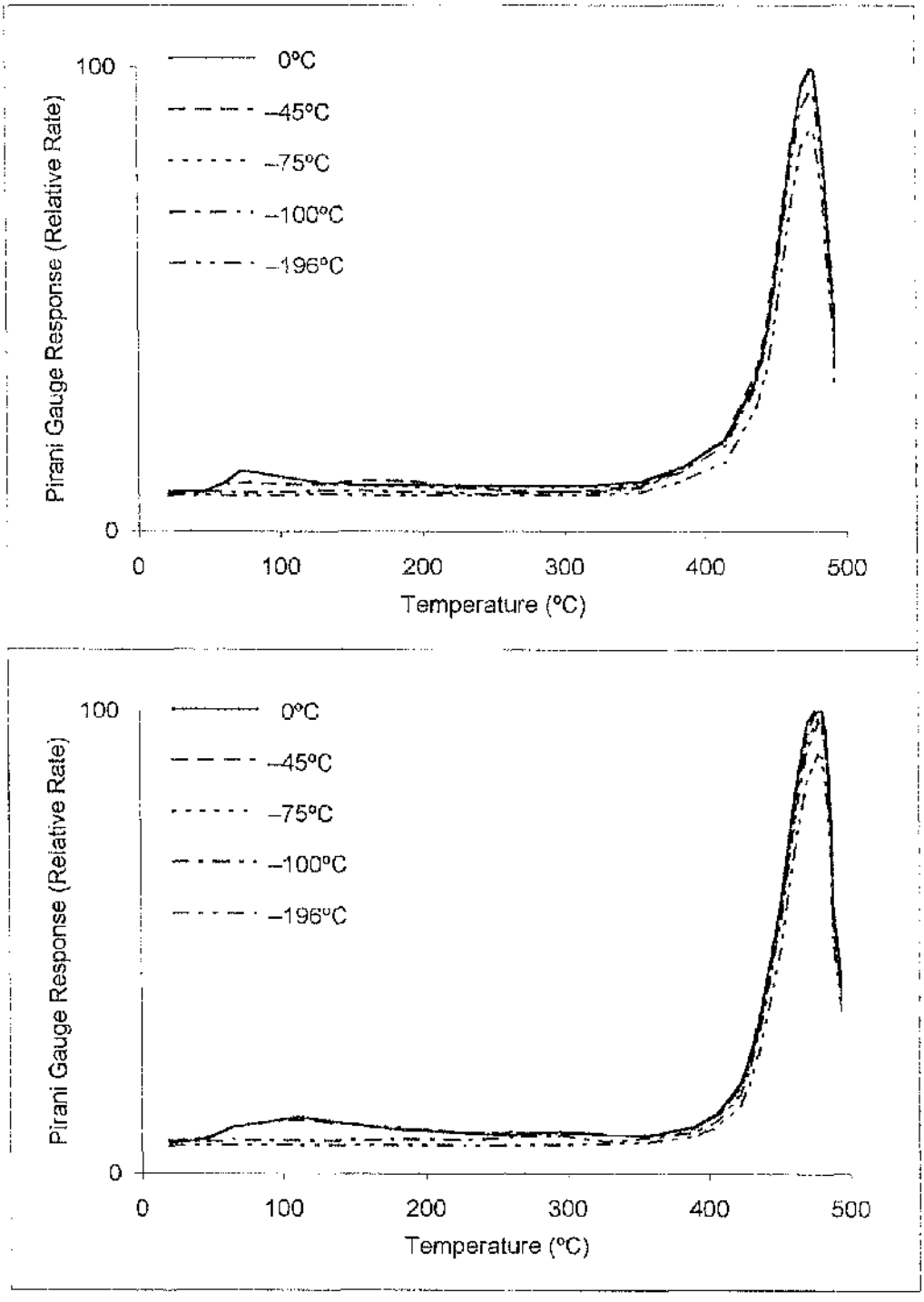


Fig. 4.9 TVA curves (heating rate10°C/min to 500°C) obtained for zinc polyacrylate made by polymerisation (top) and neutralisation (bottom).

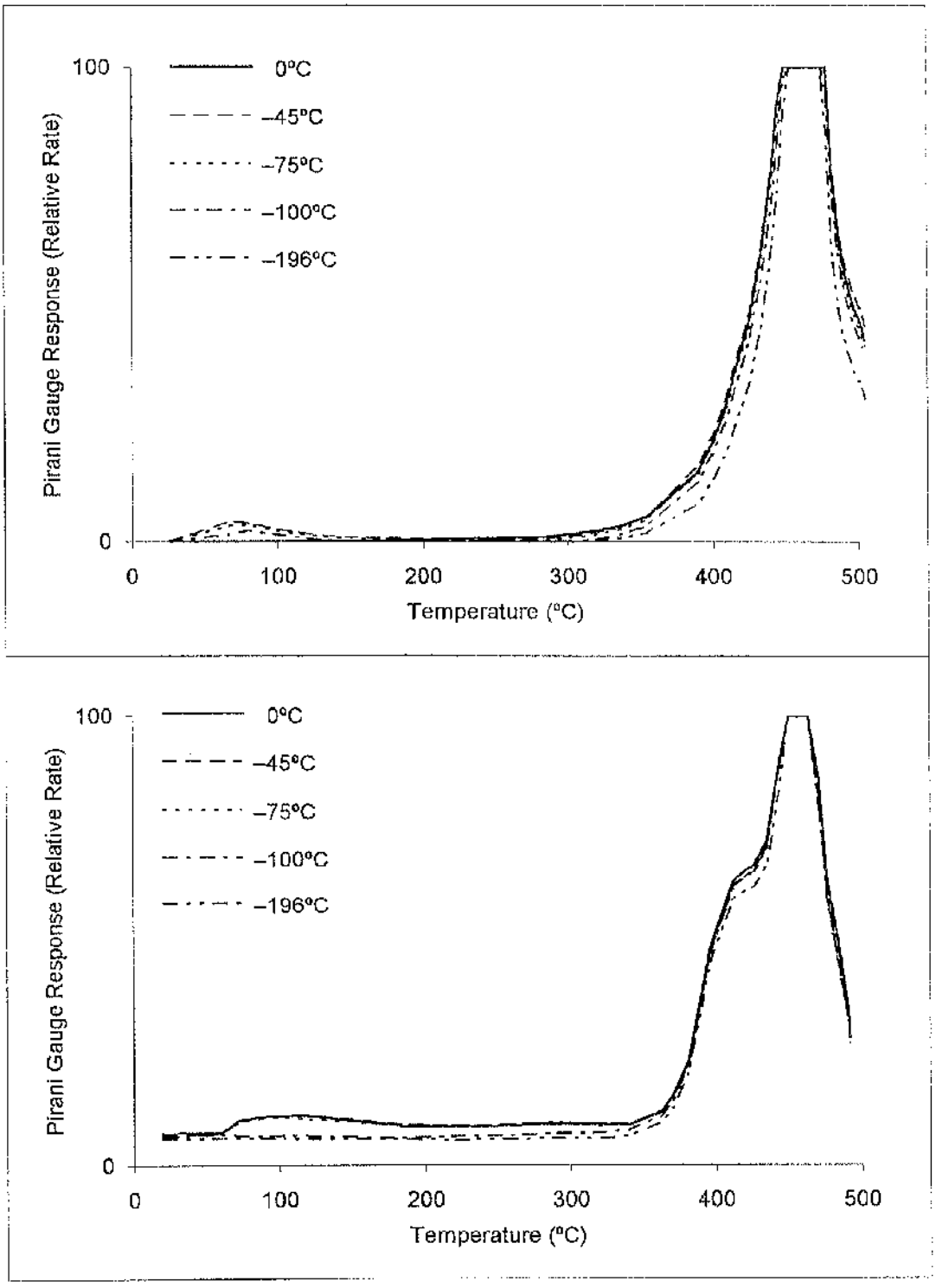


Fig. 4.10 TVA curves (heating rate 10°C/min to 500°C) obtained for cobalt polyacrylate made by polymerisation (top) and neutralisation (bottom).

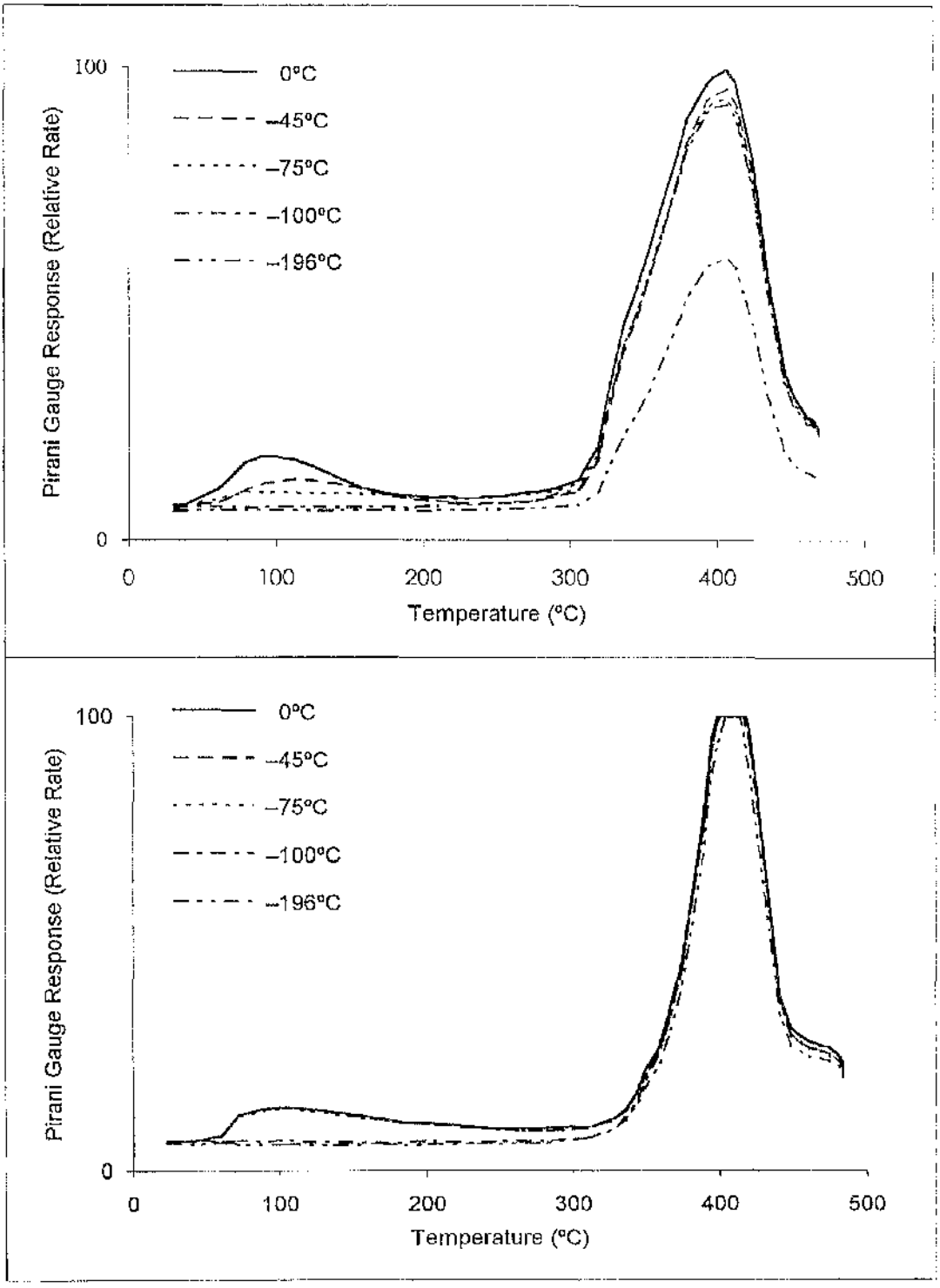


Fig. 4.11 TVA curves (heating rate 10°C/min to 500°C) obtained for nickel polyacrylate made by polymerisation (top) and neutralisation (bottom).

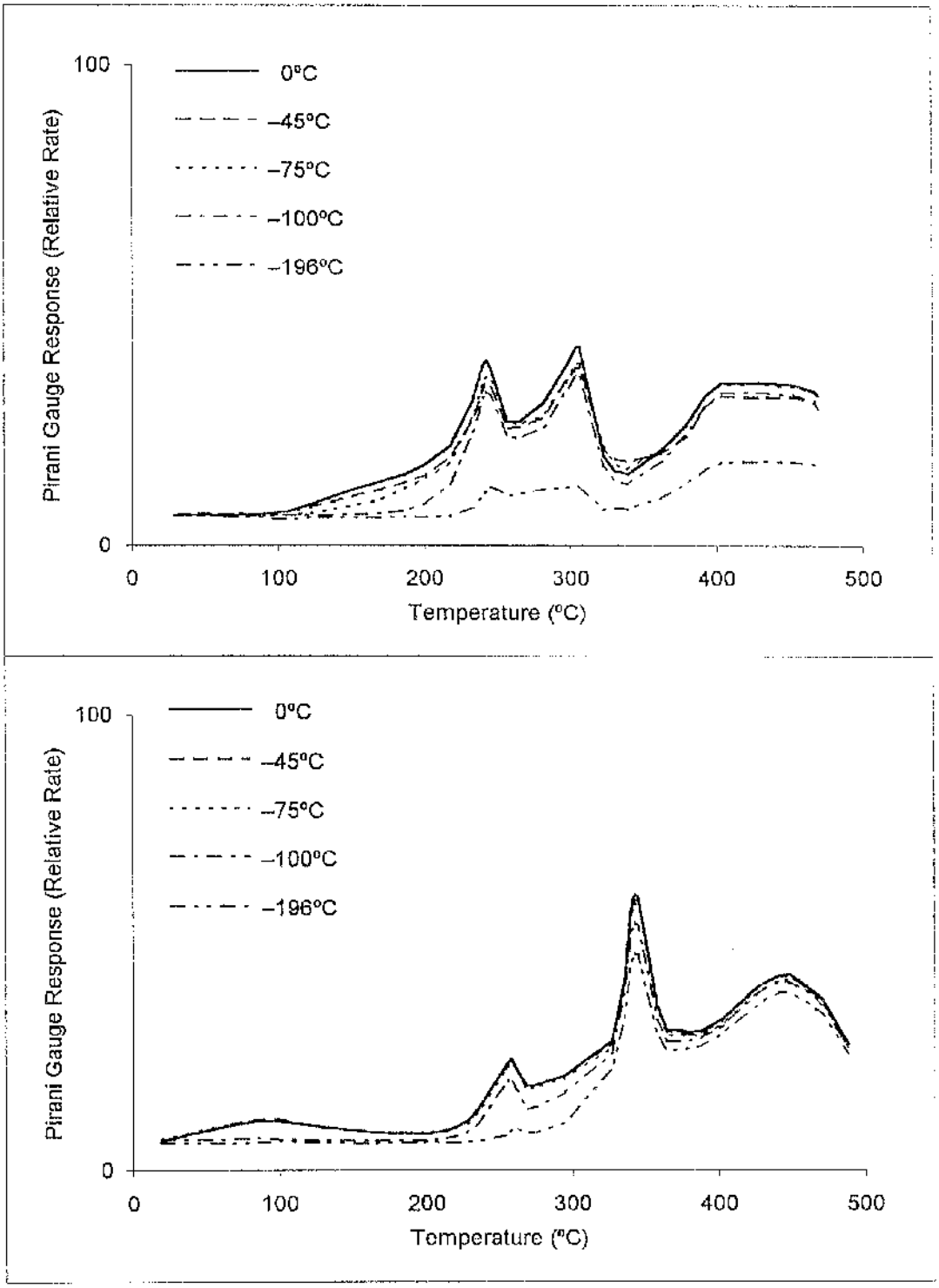


Fig. 4.12 TVA curves (heating rate 10°C/min to 500°C) obtained for copper polyacrylate made by polymerisation (top) and neutralisation (bottom).

	T_{onset}	T_{max}	% weight of residue at 500°C	% weight of crf
zinc polyacrylate	350°C	474°C	39.4%	–
zinc polyacrylate*	350°C	463°C	38.3%	–
cobalt polyacrylate	350°C	457°C	47.4%	–
cobalt polyacrylate*	350°C	456°C	39.8%	–
nickel polyacrylate	300°C	405°C	45.6%	6.4
nickel polyacrylate*	310°C	407°C	39.6%	5.1
copper polyacrylate	110°C	242, 307, 409°C	55.4%	13.7
copper polyacrylate*	210°C	258, 343, 443°C	37.2%	12.5

Table 4.3 TVA data for metal salt homopolymers of poly(acrylic acid).

* Polymers made by neutralisation of poly(acrylic acid)

4.5 THE IDENTIFICATION OF PRODUCTS OF POLYMER DECOMPOSITION

4.5.1 Non-condensable Gases

The products not condensable at -196°C were identified by sampling at frequent intervals using a bleed to the mass spectrometer connected to the vacuum line.

In the cases of the zinc, cobalt and nickel polymers, non-condensable gases were evolved only during the major degradation step. The results obtained for these samples follow the same pattern. The first non-condensable gas observed is carbon monoxide which is followed by hydrogen. These gases remain the only two products until the temperature approaches 450-500°C, near the end of polymer decomposition, when the amount of carbon monoxide, relative to hydrogen, decreased and trace amounts of methane were sometimes observed. Positive identification of methane was hampered by the small amount of sample and by peaks coincident with other products.

In the case of copper polyacrylate the first peak of non-condensable gases consisted entirely of carbon monoxide. Hydrogen is evolved, in addition to carbon monoxide, in the second and third peaks with trace amounts of methane observed in the final stage of degradation.

In copper polyacrylate, prepared by neutralisation of poly(acrylic acid), the first peak consisted of only a very small amount of carbon monoxide. The second and third peaks had larger amounts of non-condensable gases with hydrogen and carbon monoxide appearing in both and a trace amount of methane in the final peak.

4.5.2 Sub-Ambient Thermal Volatilisation Analysis

The technique of sub-ambient thermal volatilisation analysis, as described in chapter 2.2, was used to help in the partial separation and identification of the products collected in the traps on the vacuum line. The methods used in identifying the products were on-line mass spectroscopy, FT-IR spectroscopy and GC-MS. The SATVA traces obtained are given in **Figs. 4.13** to **4.16** with the products identified being listed in **Tables 4.5** to 4.12.

The degradation products obtained from the polymers were similar in all cases. A general description of the products found in the various sections of the sub-ambient analyses is given below, with the particular products for each polymer listed in the products tables.

The SATVA traces can be split into three sections. The first are due to compounds which are gases at room temperature and achieve good enough separation by SATVA for collection in gas cells and identification by FT-IR. The second group of compounds are low boiling volatile organic compounds which can be examined in the gas phase by their infra-red spectra. They are not retained long enough in the gas chromatograph for separation from the extraction solvent and mass spectroscopy identification. The final group of compounds are higher boiling liquids, not separated by SATVA, that are collected together for separation and identification by GC-MS.

Ethene was the first substance evolved and was found as a minor degradation product of all of the polymers.

The large peak found between 10 and 15 minutes, from its infra-red (**Fig. 4.17**) and mass spectra (**Fig. 4.19**), was due to propene, ketene and carbon dioxide. The strong infra-red absorptions at 3729, 3625

2380-2320 cm^{-1} show that carbon dioxide is the major component of the peak. The absorptions for propene are the olefinic C-H stretching and bending at 3084 cm^{-1} and 912 cm^{-1}, saturated C-H stretching at 2967 cm^{-1} and C=C stretch at 1652 cm^{-1}. Two absorptions due to ketene are at 2163 cm^{-1} and 2137 cm^{-1}.

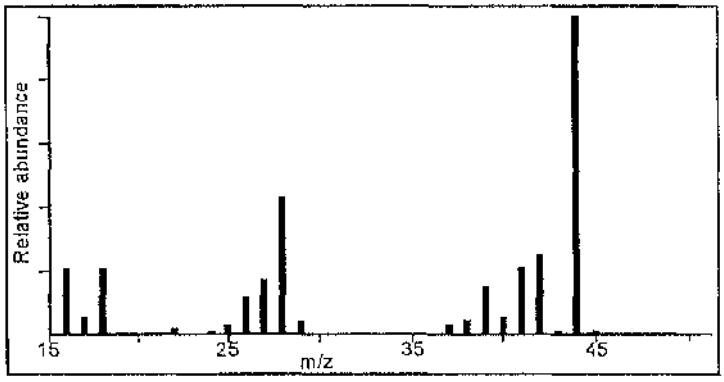


Fig. 4.19 Mass spectrum of degradation products found between 10 and 15 minutes in SATVA.

Acetylene, butene and 1,3 pentadiene were also found as minor products in some of the samples. The appropriate butene isomer or isomers formed were not identifiable by mass spectroscopy and there was not enough sample for infra-red identification.

The next group of products evolved between, 15-20 minutes, consisted of compounds having a prominent carbonyl absorption in their infra-red spectrum (**Fig. 4.18**). The major substances positively identified were usually acetaldehyde or acetone, with acrolein found as an occasional minor product. Other ketones were identified in this area, during the SATVA analysis of the degradation products of the alkali and alkaline earth polyacrylates,[34,35] but none were observed in these experiments by infra-red or mass spectroscopy and co-elution with ether solvent made GC/MS identification impossible.

After these compounds came benzene and toluene. Toluene and occasionally benzene were able to be identified by GC-MS analysis of the liquid fraction, so the subsequent products in the largest peak of the SATVA trace were collected for GC-MS analysis.

The GC-MS results obtained are given in **Figs. 4.20** to **4.27**. The types of column, gas chromatograph and mass spectrometer used are described in chapter 2.7.

The main component of the liquid fraction was water, but due to the large amount of absorbed water in the starting polymers it was not possible to say what percentage of the liquid fraction was due to polymer degradation. Due to the very small amount of organic compounds obtained, it was not possible to separate the organic layers from aqueous for weighing. From visual examination of each sample it was estimated that the water content was always over 95%. The amount of organic compounds varied for each of the polymers. The cobalt polymers, compared to the other metals, gave only a very small amount of sample for GC-MS analysis.

Although the total amount of organic products appeared to vary with the metal ion involved, all the samples gave large numbers of different products, many of which were too small in amount for identification.

The majority of compounds found by GC-MS analysis were aromatic with fewer ketones identified. Acrylic acid was rarely seen, except in the case of zinc polyacrylate where it was the major product. No other carboxylic acid-containing compounds were found. A number of minor products eluted before benzene were not identifiable.

The ketones identified were based mainly on cyclic five member carbon structures with the occasional six membered rings, most containing carbon-carbon double bonds.

The simple alkyl substituted aromatics, toluene, xylene isomers and styrene were the major products found in the gas chromatograms of all of the polymers. A wide range of other alkyl substituted aromatic compounds were also found as more minor products. These consisted of mono-, di- and tri-substituted phenyls, with both saturated and unsaturated groups, of up to four carbon atoms

A number of oxygen-containing aromatic compounds also were identified. These consisted of mono- and di-hydroxy substituted phenyl and alkyl substituted phenyl compounds, benzofurans and some aromatic aldehydes and ketones.

Possible reaction mechanisms that result in the formation of these compounds are discussed in section 4.6.

4.5.3 Degradation Residue

For all the polymers the residue of degradation was a black solid consisting of metal oxide and a carbonaceous residue. The amounts of residue, expressed as fractions of the total starting weights are given in **Table 4.3**. The infra-red spectra of the residues are given in **Figs. 4.28a** to **4.28d**.

Smaller amounts of residue were obtained for the zinc polymers compared to their TG results. These were 39.4% and 38.3% for the polymers made by polymerisation and neutralisation respectively, compared to the TG results of 54.5% and 49.7%. This is due to the volatility under vacuum of zinc, at the elevated degradation temperatures,

collected as a product in the cold ring fraction. It was formed by zinc oxide decomposition in the presence of carbon found in the residue, The amount of zinc oxide in the degradation residue was still considerable at 59% of the total residue weight.

The infra-red spectra of the cobalt, nickel and copper residues are dominated by the absorptions due to the large metal oxide content. In these polymers all the metal remained in the residue, mostly in the form of the metal(II)oxide, but copper(I)oxide was also identified. The infra-red spectra show no absorptions associated with metal carboxylates or carbonates. None of the constituents of the carbonaceous residue were identified.

Due to the smaller metal oxide content of the zinc residue an absorption can be seen at 3060 cm^{-1} due to aromatic C-H stretching. Bands at 2923 $cm,^{-1}$ 2853 cm^{-1} and 1384 cm^{-1} are characteristic of saturated C-H absorptions due to remaining chain fragments. The two prominent, broad bands at 1600 cm^{-1} and 1420 cm^{-1} may be due to undecomposed carboxylate groups. A series of absorptions between 900 cm^{-1} and 750 cm^{-1} suggest the presence of aromatic compounds.

The large absorption at 629 cm^{-1} in the copper residue spectrum is characteristic of Cu_2O.[61] Occasionally copper metal was formed as a degradation product. At the degradation temperatures, reduction of copper oxide to copper by carbon in the carbonaceous residue would give copper(I)oxide as an intermediate in the reaction.

4.5.4 Cold Ring Fraction

After the polymers were degraded to 500°C the products barely volatile at the degradation temperatures, termed the cold ring fraction, were collected by condensation by the water cooled jackets described in

chapter two. No observable cold ring fraction was obtained for the cobalt polymers and only a trace amount was collected from the zinc polymers.

Larger amounts of cold ring fraction were obtained for the nickel and copper polymers. These amounted to 6.4% and 5.1% of the total starting weight of the nickel polymers made by polymerisation and neutralisation respectively, and 13.7% and 12.5% for the corresponding copper polymers.

The cold ring fraction consisted of a brown waxy solid soluble in dichloromethane but only partially soluble in methanol. The cold ring fractions were analysed by studying their infra-red and mass spectra.

The infra-red spectra of the cold ring fractions obtained from the nickel and copper polyacrylates are given in **Figs. 4.29a** to **4.29d**.

The infra-red spectra for the nickel polymers (**Fig 4.29a** & **b**) made by polymerisation and neutralisation are the same. No evidence for the presence of monomer was observed and the most prominent features of the spectrum can be assigned to absorptions due to carboxylic acid groups. These include the carboxylic acid carbonyl stretching at 1705 $cm,^{-1}$ O-H stretching between 3600 cm^{-1} and 2800 $cm,^{-1}$ O-H bending at 1378 cm^{-1} and C-O stretching at 1266 $cm.^{-1}$

The absorptions at 3055 $cm,^{-1}$ 3024 cm^{-1} and a series of bands from 1000-750 cm^{-1} are due to unsaturated or aromatic C-H absorptions. Further evidence for the presence of aromatic compounds is the band at 1603 $cm,^{-1}$ and a partially obscured absorption at 1495 cm^{-1} due to C-C aromatic ring stretching.

The peak assignments for the infra-red spectrum of copper polyacrylate (**Fig 4.29c**) are similar to those for nickel polyacrylate. The absorptions at 1705 cm^{-1} and 1266 cm^{-1} are due to the carboxylic acid carbonyl and C-O stretching bands, while the O-H stretching and bending absorptions appear at 3600-2800 cm^{-1} and 1377 $cm.^{-1}$

The infra-red spectrum of copper polyacrylate* (**Fig. 4.29d**) is similar to the above but with bands at 1803 cm^{-1} and 1758 $cm.^{-1}$ These are thought to be due to acid anhydrides present in the cold ring fraction. The position and the greater intensity of the lower frequency band suggest that these are six member glutaric anhydride structures similar to those obtained in the degradation of poly(acrylic acid).[29]

Although the infra-red spectrum suggests the presence of large numbers of carboxylic acid groups a proportion of the cold ring was not soluble in polar solvents such as propanol and methanol.

The mass spectra of the cold ring fractions of nickel polyacrylate and both copper polyacrylates were also recorded (**Fig 4.30a** to **4.30c**). The large numbers of peaks found, indicated that there were many different degradation products in the cold ring fraction with molecular weights up to approximately 300 amu.

The prominent peak seen at (m/z)=91 would suggest the presence of aromatic compounds. This is in agreement with the infra-red spectrum, but it was not possible to identify any from their molecular ion or fragmentation patterns due to the large numbers of peaks found in the spectra.

The results obtained from infra-red and mass spectral analysis indicate that the cold ring fraction consists of carbon chains containing different numbers of carboxylic acid side groups and also smaller amounts of unidentified aromatic compounds.

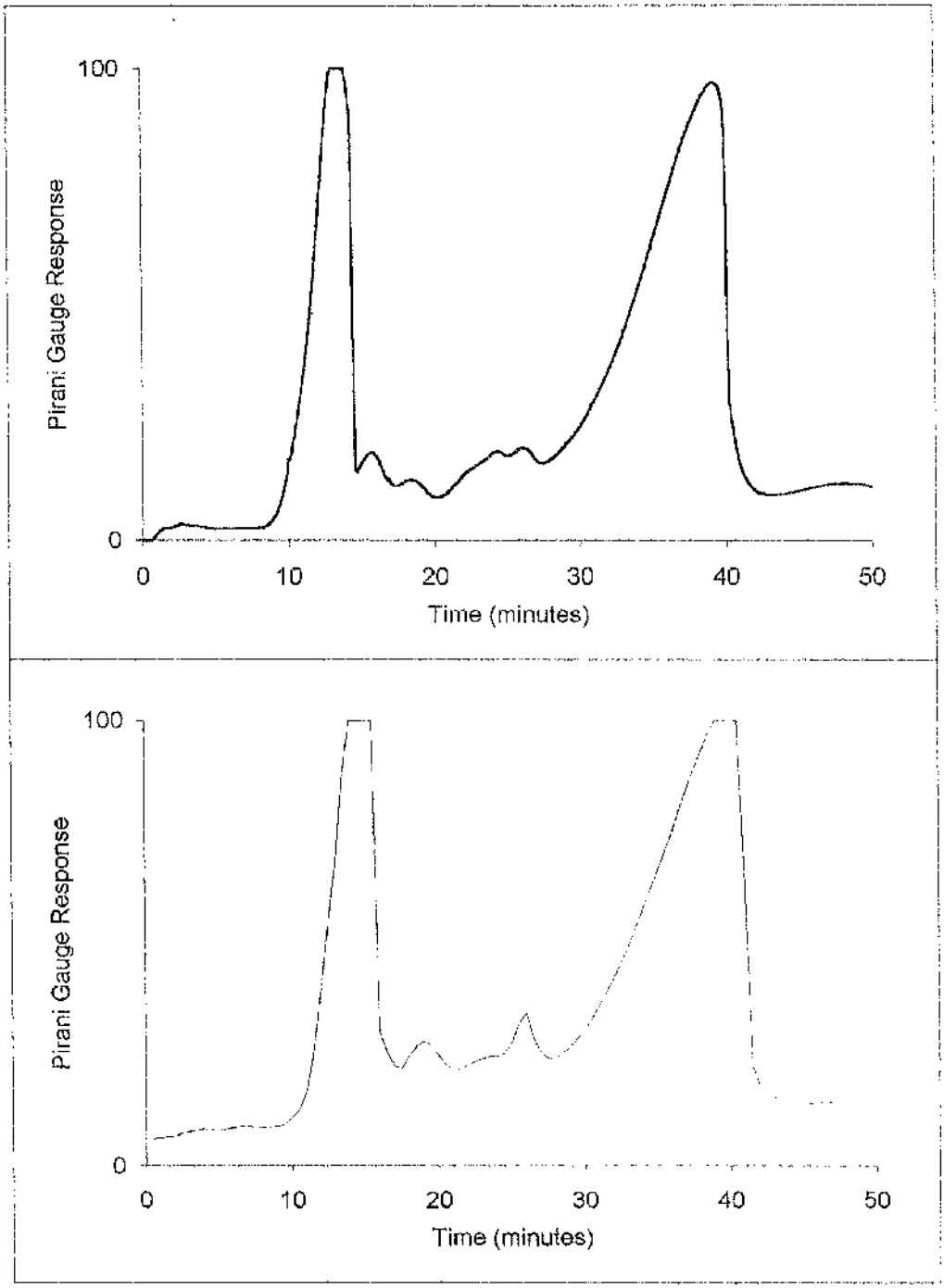


Fig. 4.13 SATVA curves of the products of degradation, obtained under TVA conditions, of zinc polyacrylate, made by polymerisation (top) and neutralisation (bottom).

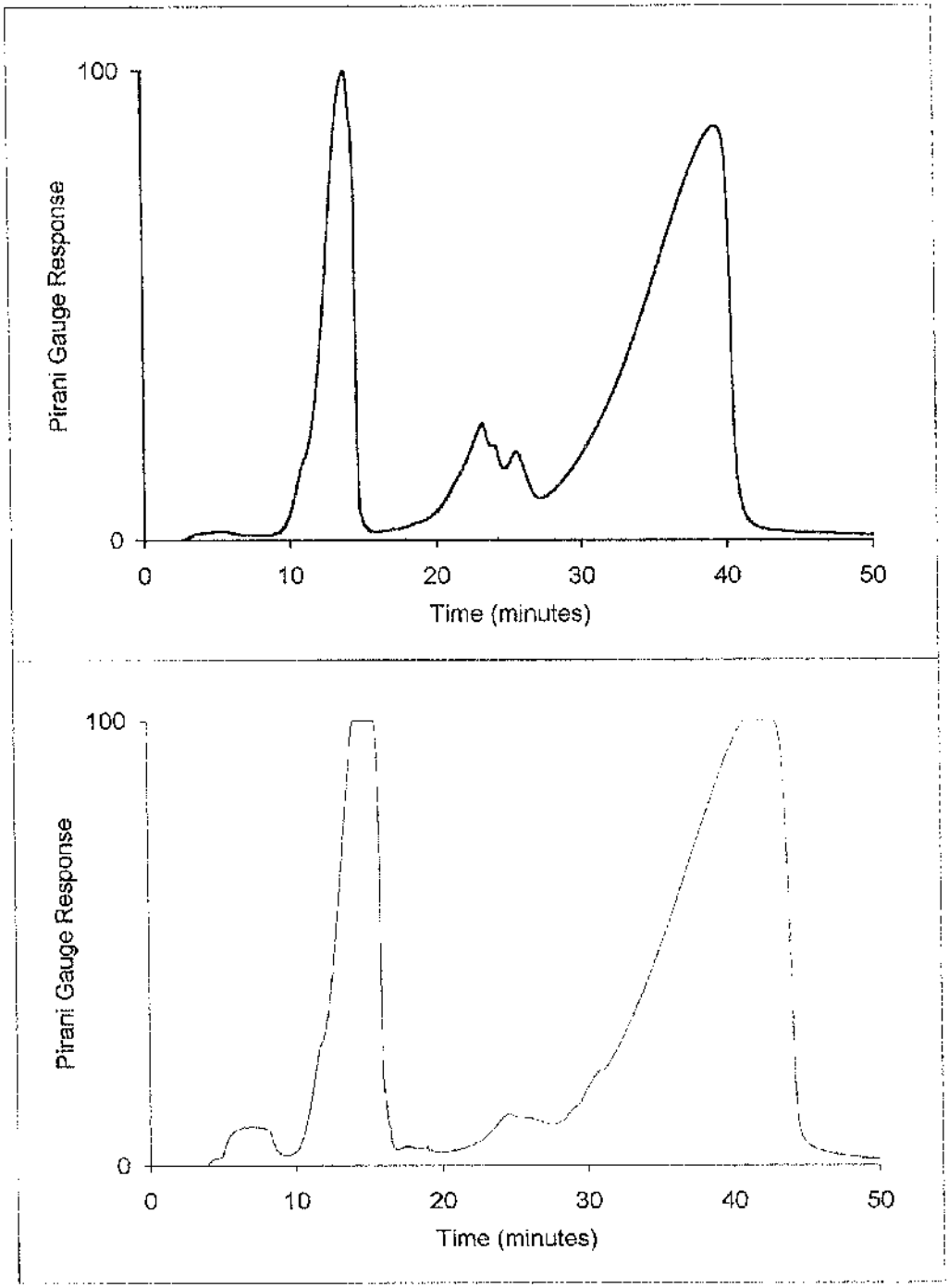


Fig. 4.14 SATVA curves of the products of degradation, obtained under TVA conditions, of cobalt polyacrylate, made by polymerisation (top) and neutralisation (bottom).

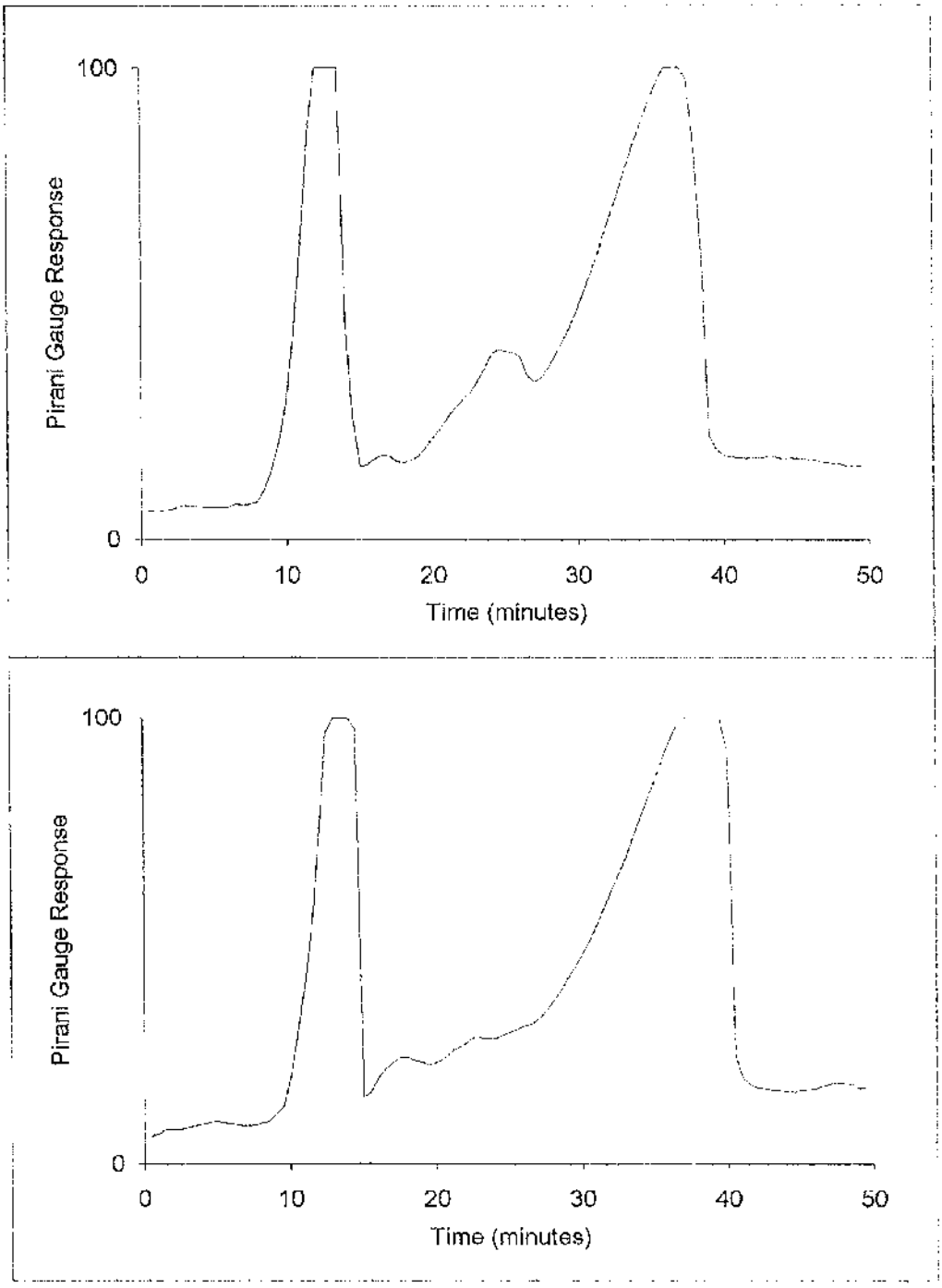


Fig. 4.15 SATVA curves of the products of degradation, obtained under TVA conditions, of nickel polyacrylate, made by polymerisation (top) and neutralisation (bottom).

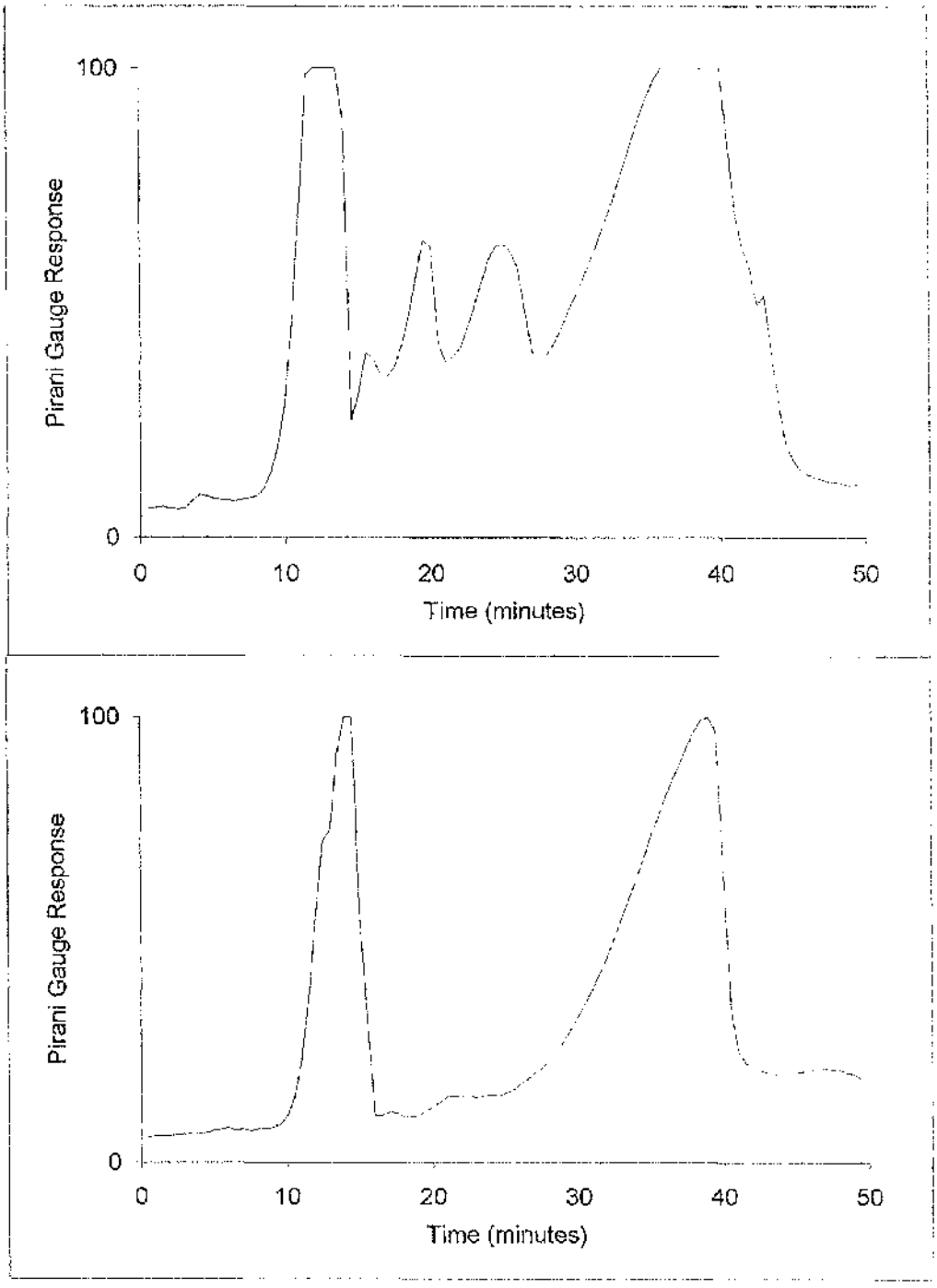


Fig. 4.16 SATVA curves of the products of degradation, obtained under TVA conditions, of copper polyacrylate, made by polymerisation (top) and neutralisation (bottom).

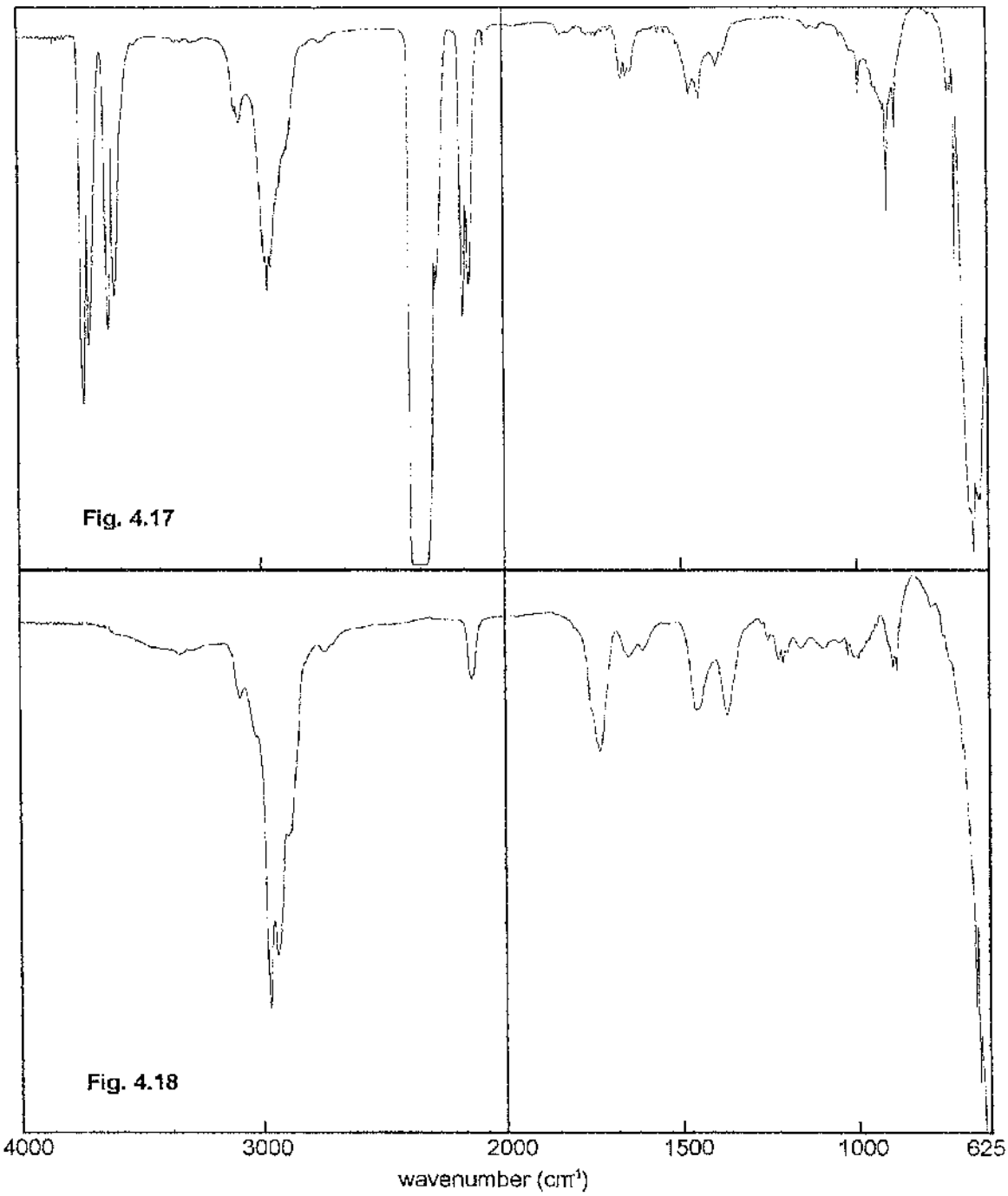


Fig. 4.17 Infra-red spectrum of substances collected between 10 and 15 minutes during SATVA.

Fig. 4.18 Infra-red spectrum of substances collected between 15 and 20 minutes during SATVA.

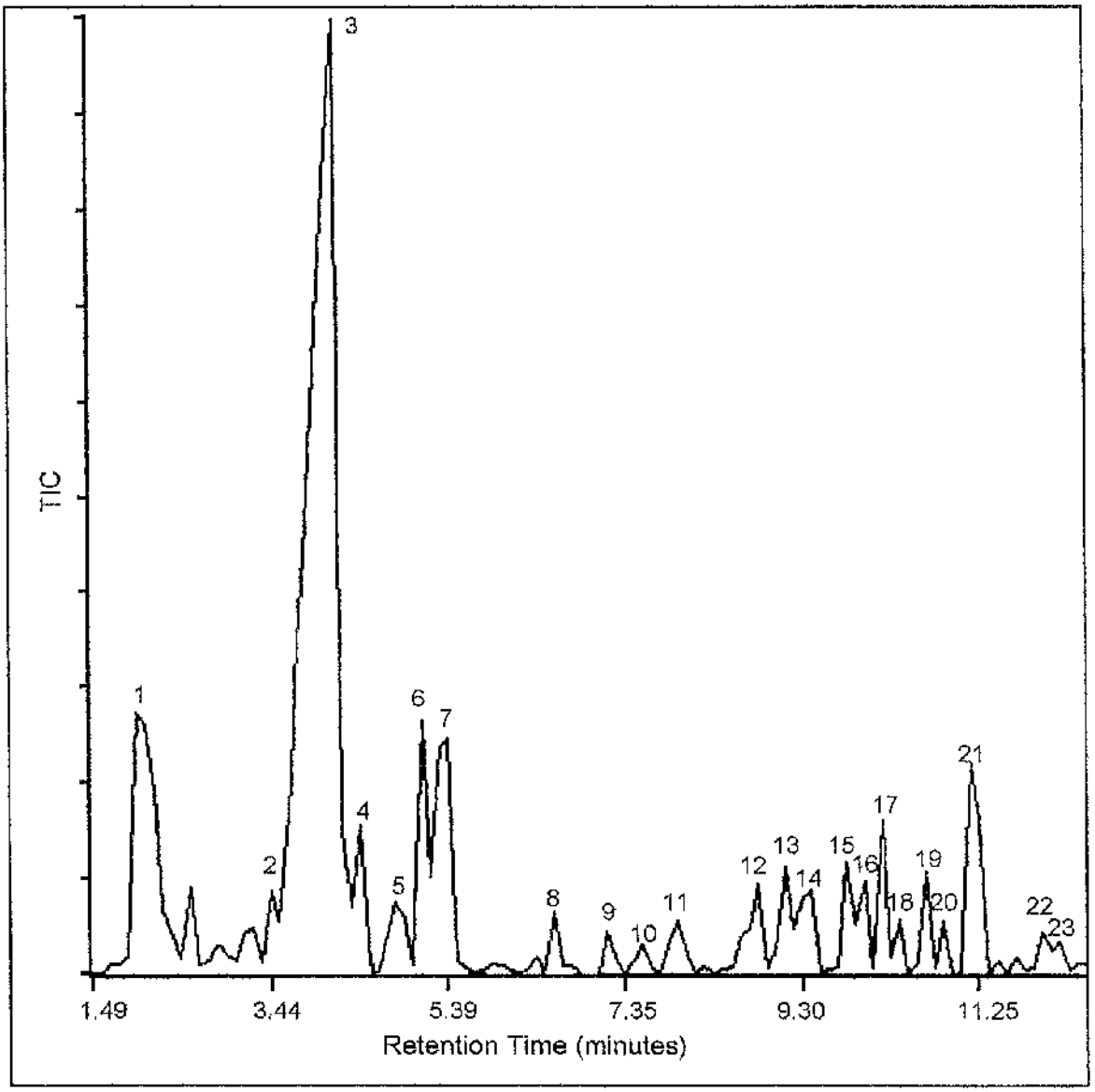


Fig. 4.20 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of zinc polyacrylate, prepared by polymerisation.

Peak Assignments

1 toluene, **2** 2-cyclopentenone, **3** acrylic acid, **4,5** xylenes, **5** 2-methylcyclopentanone, **6** styrene, **7** 2-methylcyclopent-1-enone, **8** 2,3 dimethylcyclopent-1-enone, **9** benzaldehyde, **10** propylbenzene, **11** ethyltoluene, **12** 3-methylcyclohex-2-enone, **13** benzofuran, **14** trimethylbenzene, **17** phenol, **18** ethyltoluene, **19** propenylbenzene, **20** 3-methylstyrene, **21** propynylbenzene, **22** 1-phenyl-1-propanone, **23** tolualdehyde.

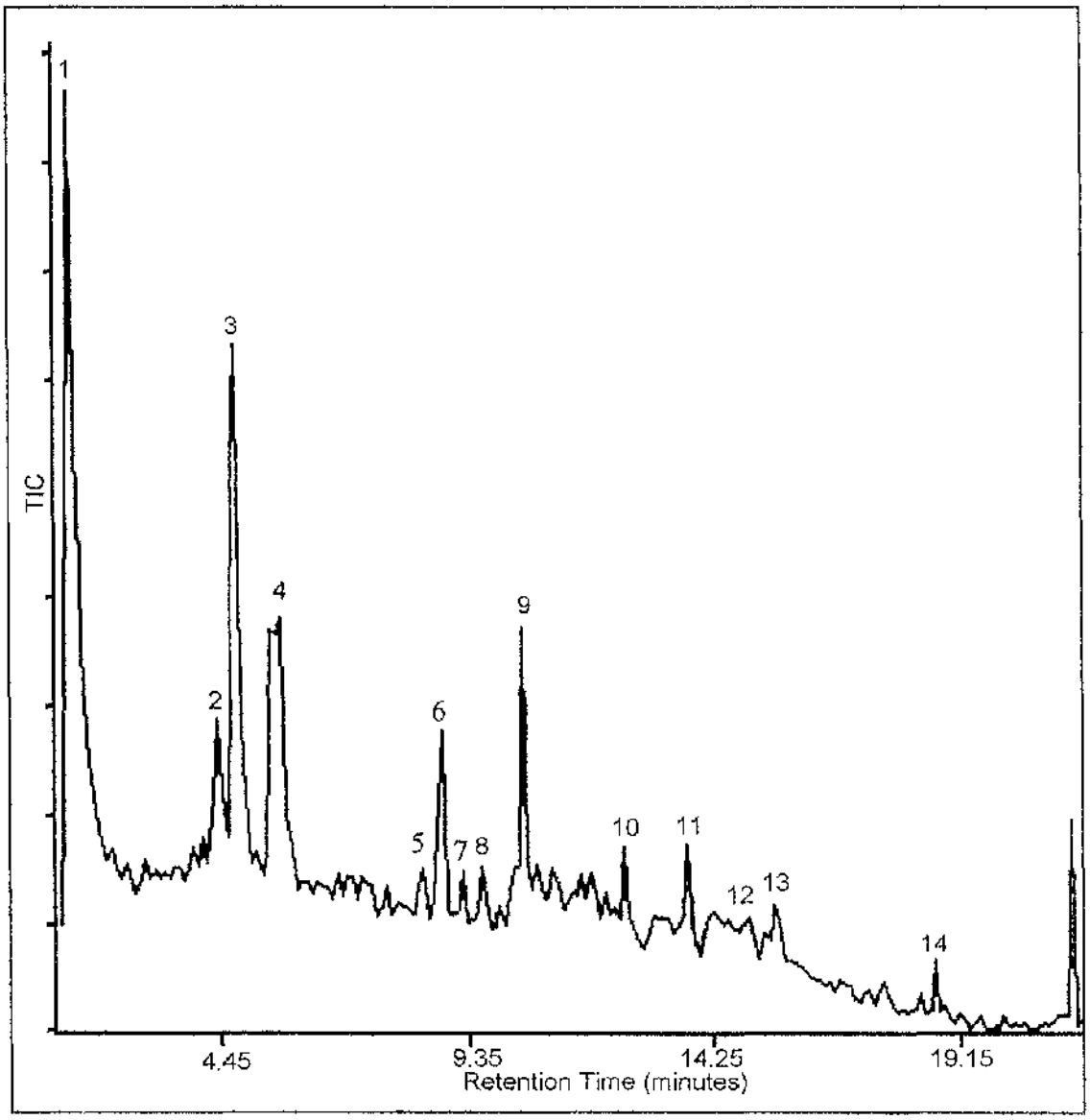


Fig. 4.21 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of zinc polyacrylate*, prepared by neutralisation.

Peak Assignments

1 toluene, **2** ethylbenzene, **3,4** xylenes, **4** styrene, **5** propylbenzene, **6** cumene, **7,8** ethyltoluene **9** α-methylstyrene **10** indene, **11** cresol, **12** 7-methylbenzofuran, **13,** 2-methylbezofuran,**14** naphthalene

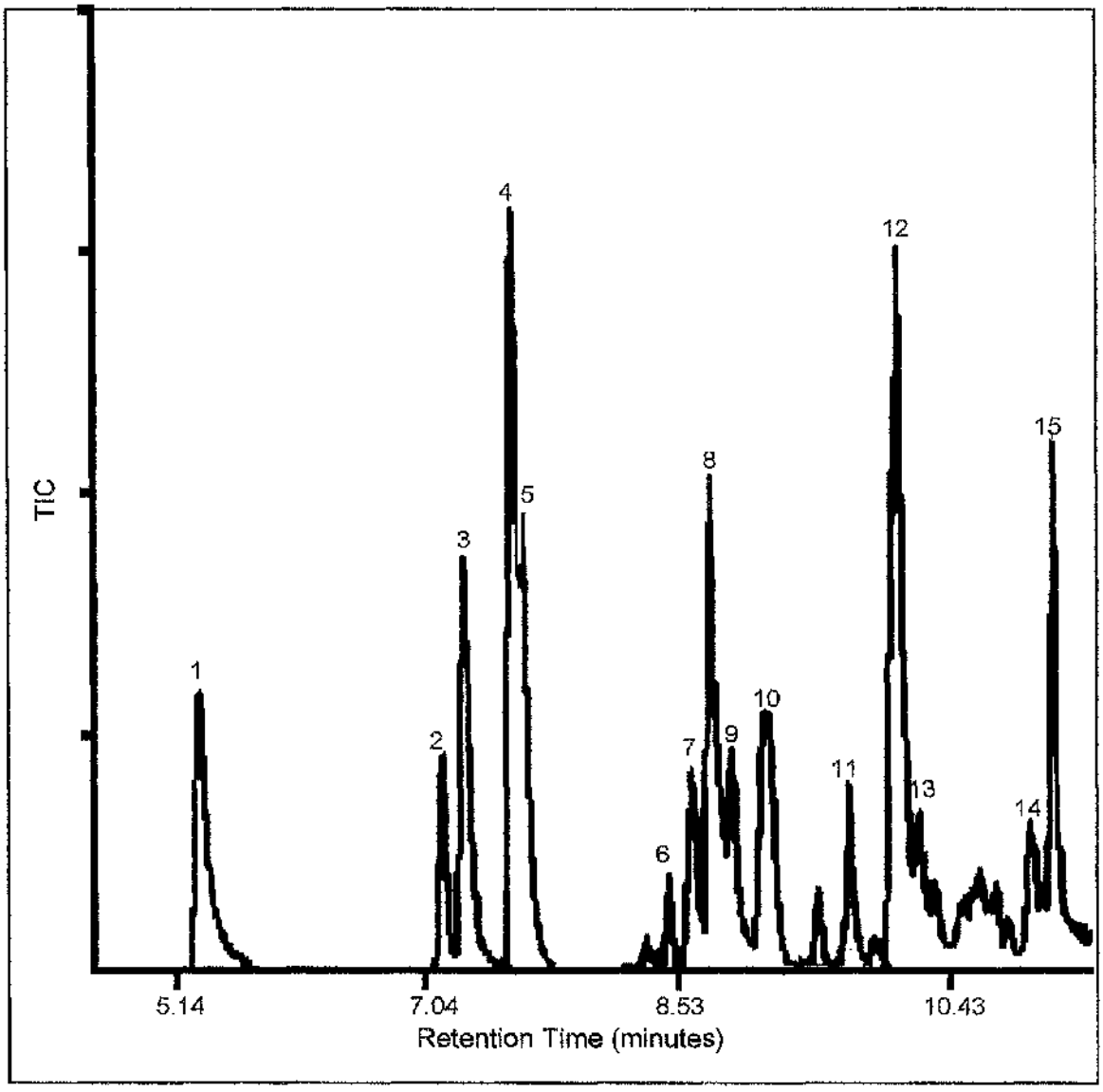


Fig 4.22 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of cobalt polyacrylate, made by polymerization.

Peak Assignments

1 toluene, **2** ethylbenzene, **3,5** xylene, **4** styrene, **6** propylbenzene, **7** ethyltoluene, **8** phenol, **9** cumene, **10** α-methylstyrene, **11** propenylbenzene, **12** o-cresol, **13** 1-phenyl-1-propanone, **14** 7-methylbenzofuran, **15** 2-methylbenzofuran.

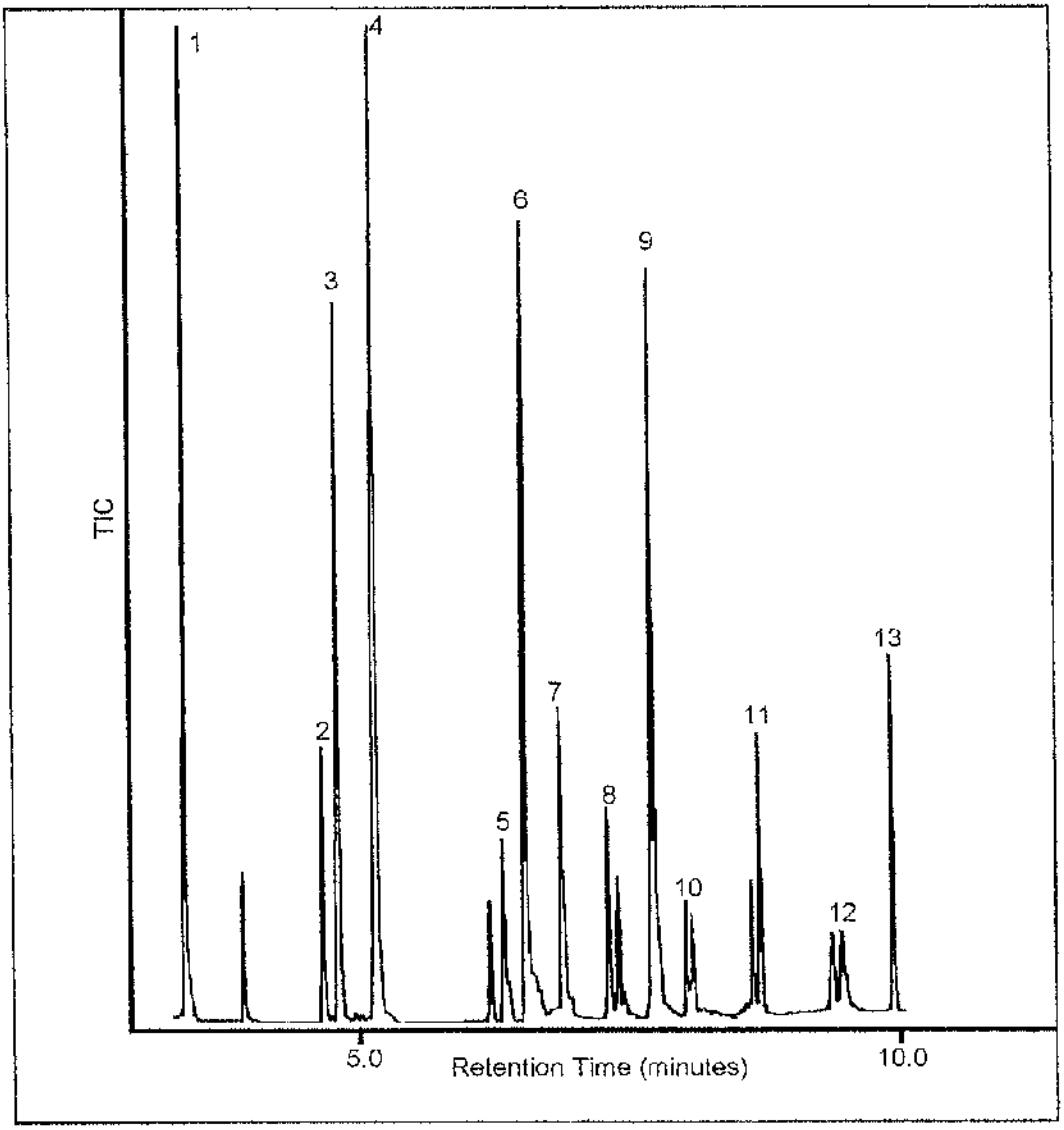


Fig. 4.23 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of cobalt polyacrylate, prepared by neutralisation.

Peak Assignments

1 toluene, **2** ethylbenzene, **3,4** xylenes, **4** styrene, **5** propylbenzene, **6** ethyltoluene, **7** 2-propenylbenzene, **8** propynylbenzene, **9** phenol, **10** cresol, **11** 1-methyl-1H-indene, **12** 2-methylbenzofuran, **13** naphthalene.

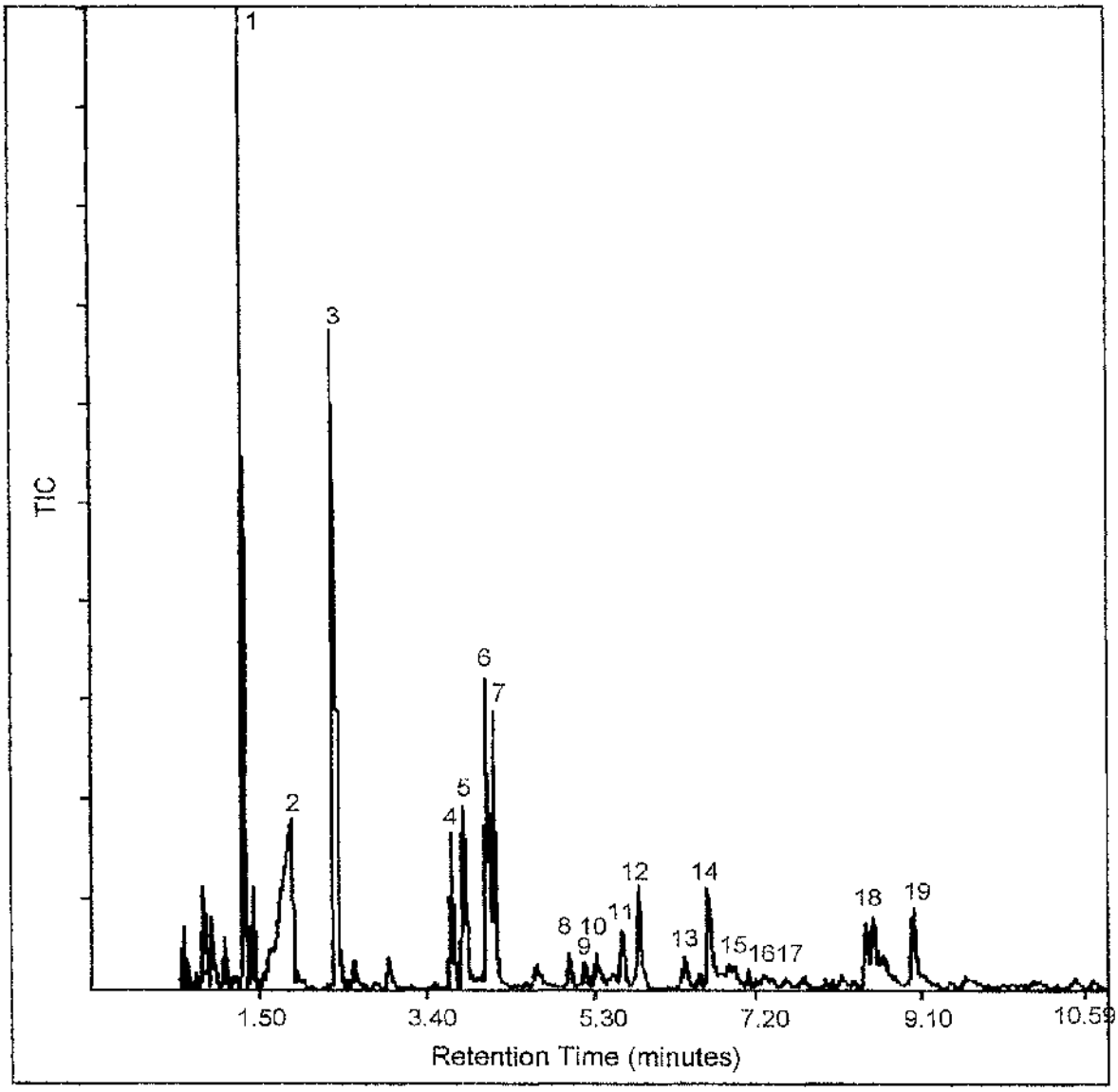


Fig. 4.24 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of nickel polyacrylate, made by polymerisation.

Peak Assignments

1 benzene, **2** acrylic acid, **3** toluene, **4** ethylbenzene, **5,7** xylenes, **6** styrene, **8** 2-propenylbenzene, **9** propylbenzene, **10** trimethylbenzene, **11** ethyltoluene, **12** 1-propenylbenzene, **13** phenol, **14** propynylbenzene, **15** butylbenzene, **16** 1-methyl-3-propylbenzene, **17** p-cresol, **18** 1-methyl-1H-indene, **19** naphthalene.

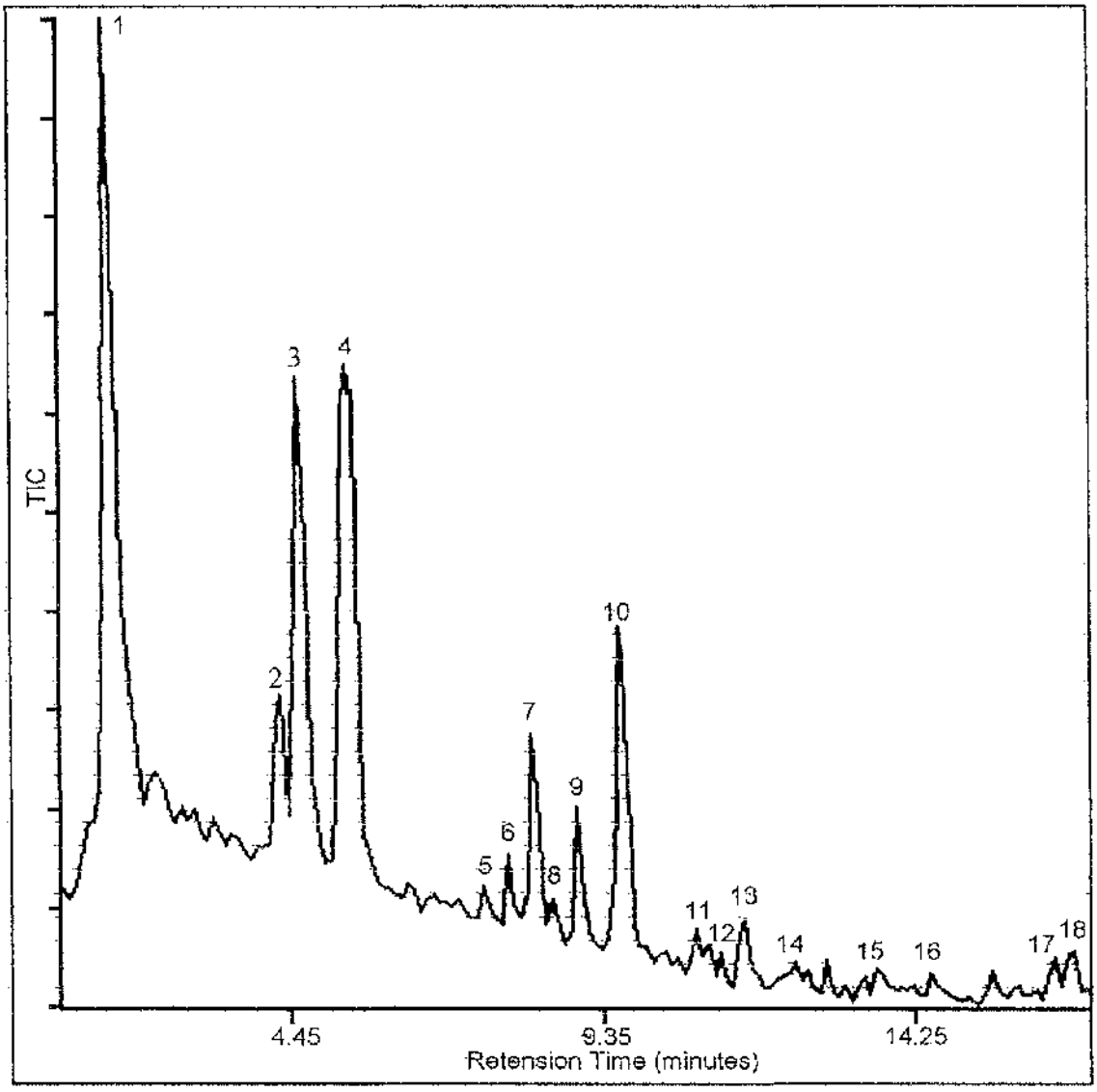


Fig. 4.25 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of nickel polyacrylate, made by neutralisation .

1 toluene, **2** ethylbenzene **3,4** xylene, **4** styrene, **5** 2-propenylbenzene, **6** propyl-benzene, **7** cumene, **8,9** trimethylbenzene, **10** phenol, **11** ethyltoluene, **12** α-methylstyrene, **13** propynylbenzene, **14** propyltoluene, **15** 7-methyl-benzofuran, **16** 2-methylbenzofuran, **17** 3-methyl-1H-indene, **18** 1-methyl-1H-indene, **19** naphthalene.

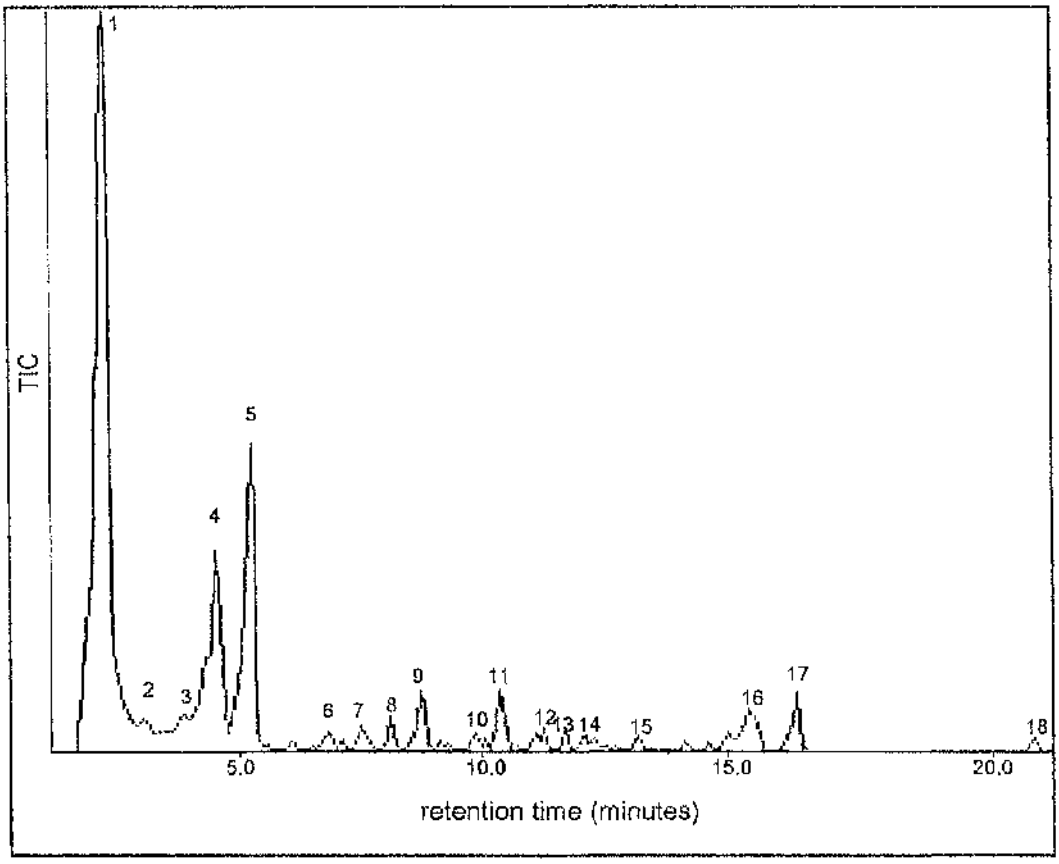


Fig. 4.26 Gas chromatrogram of liquid fraction separated by SATVA from the products of degradation to 500°C of copper polyacrylate, made by polymerisation.

Peak Assignments

1 toluene, **2** acrylic acid, **3** ethylbenzene, **4**,**5** xylenes, **5** styrene, **6** 2-propenylbenzene, **7** propylbenzene **8**,**9** trimethylbenzenes, **10** phenol, **11** propynylbenzene, **12** 1-ethyl-3-propylbenzene, **13** butylbenzene, **14** cresol, **15** 2-methylbenzofuran, **16** 1,3-butadienylbenzene, **17** naphthalene, **18** 1-methylnaphthalene.

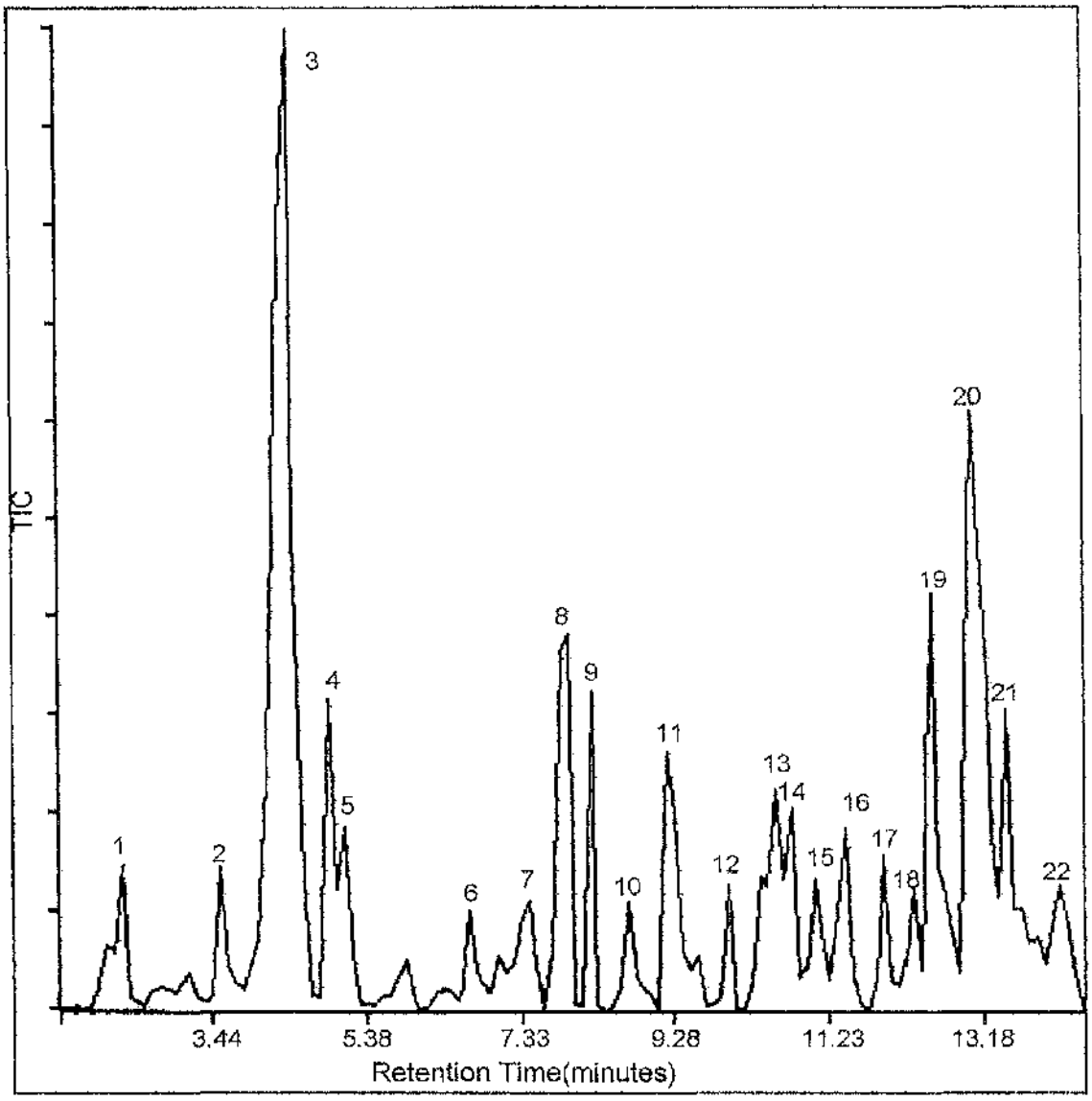


Fig 4.27 Gas chromatogram of liquid fraction separated by SATVA from the products of degradation to 500°C of copper polyacrylate*, made by neutralisation.

Peak Assignments

1 toluene, **2** acrylic acid, **3,4** xylene, **4** styrene, **5** 2-methylcyclo- pent-2-enone, **6** 2,3 dimethylcyclopent-2-enone, **7** propylbenzene, **8,9** trimethylbenzene, **10** 3 methylcyclohex-2-enone, **11** propenylbenzene(E), **12** 2,4,4-trimethyl-2-butenolide **13,19 & 21** unknown **14** 1-propenylbenzene, **15** indene, **16**, **17** methylpropylbenzene, **18** ethyldimethylbenzene, **20** cresol **22** 2-methylbenzofuran.

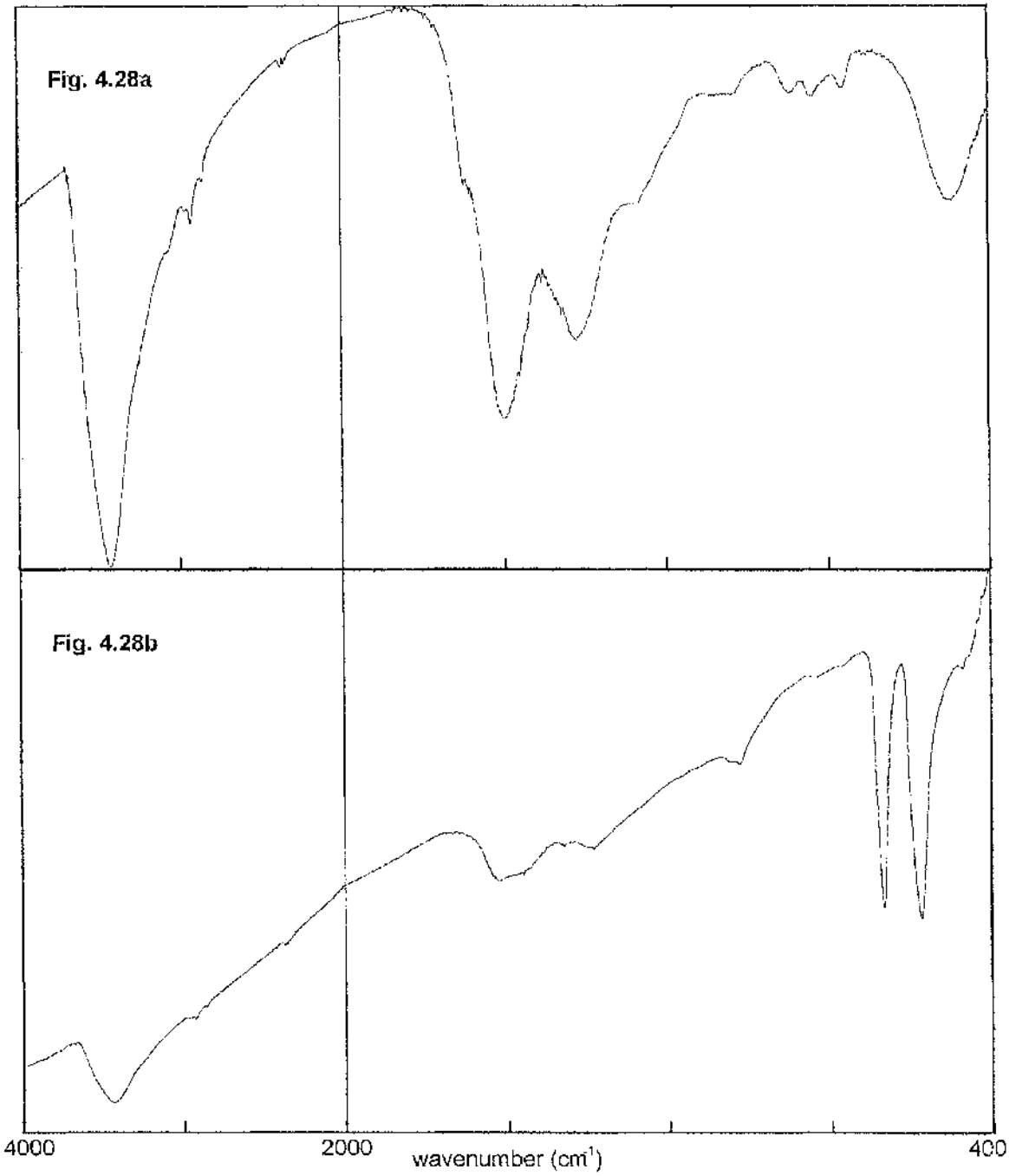


Fig. 4.28a Infra-red spectrum of the residue of degradation, under TVA conditions, of zinc polyacrylate.

Fig. 4.28b Infra-red spectrum of the residue of degradation, under TVA conditions, of cobalt polyacrylate.

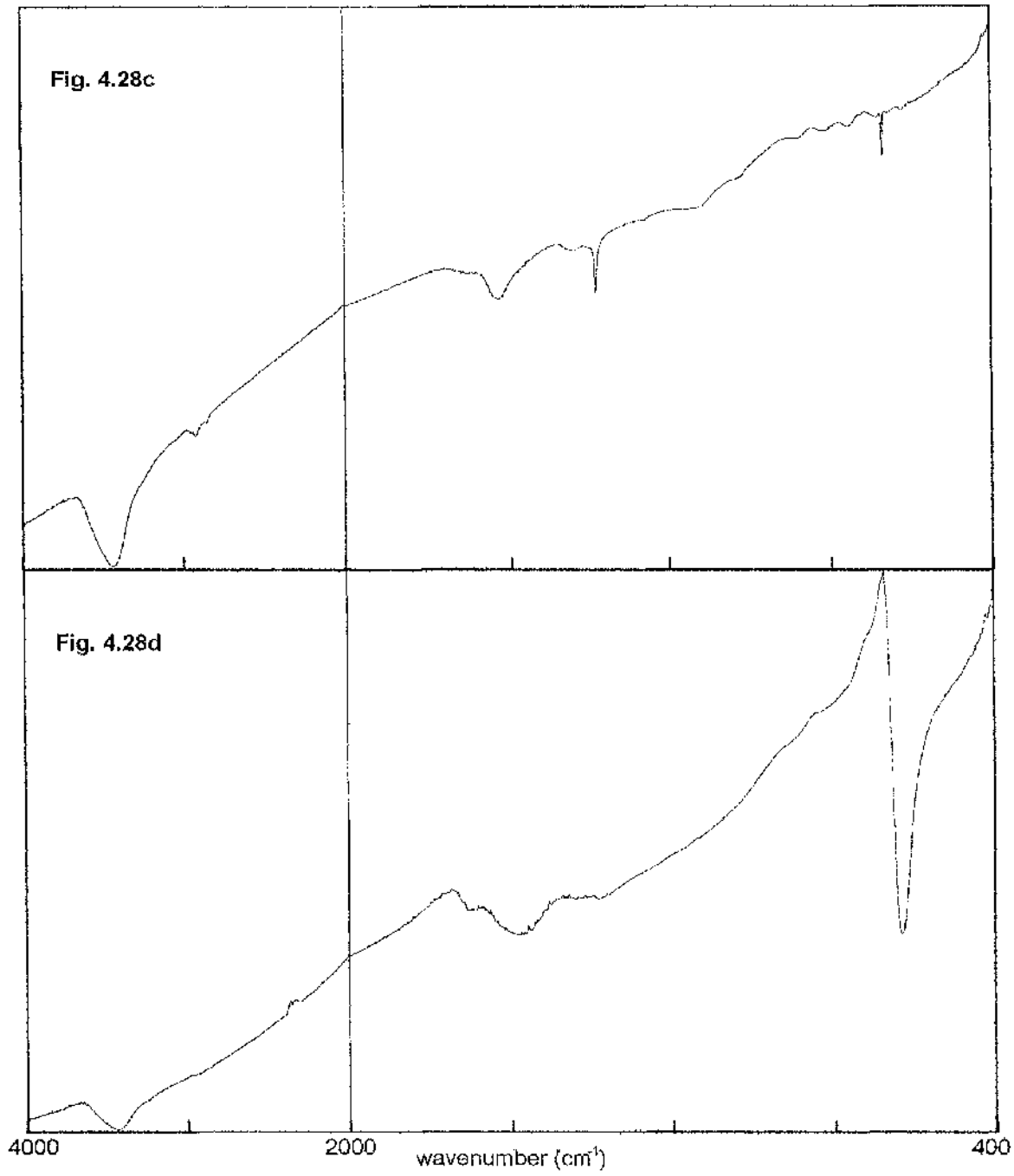


Fig. 4.28c Infra-red spectrum of the residue of degradation, under TVA conditions, of nickel polyacrylate.

Fig. 4.28d Infra-red spectrum of the residue of degradation, under TVA conditions, of copper polyacrylate.

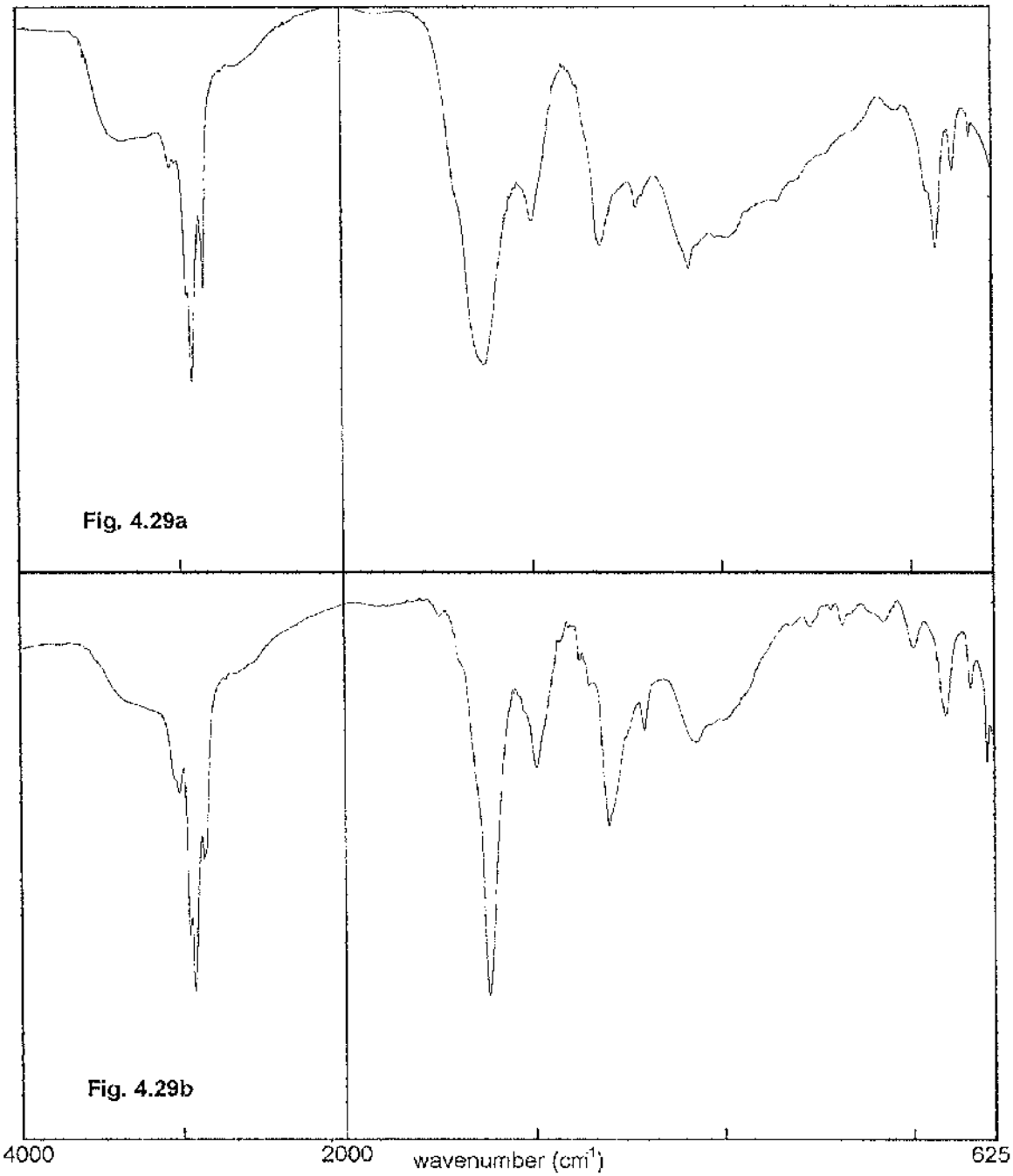


Fig. 4.29a Infra-red spectrum of cold ring fraction from degradation, under TVA conditions, of nickel polyacrylate.

Fig. 4.29b Infra-red spectrum of cold ring fraction from degradation, under TVA conditions, of nickel polyacrylate.*

* made by neutralisation

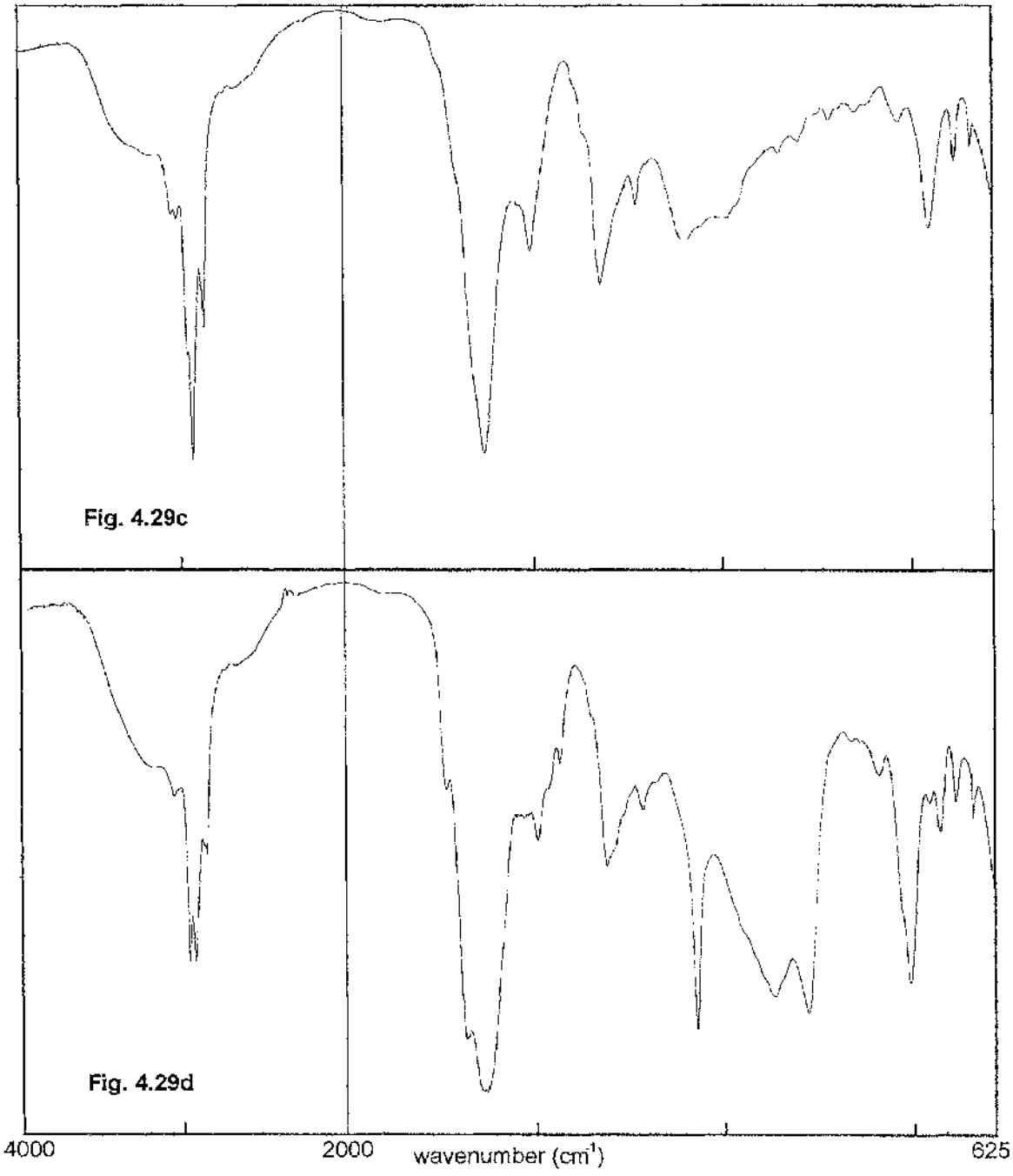


Fig. 4.29c Infra-red spectrum of cold ring fraction from degradation, under TVA conditions, of copper polyacrylate.

Fig. 4.29d Infra-red spectrum of cold ring fraction from degradation, under TVA conditions, of copper polyacrylate.*

* made by neutralisation

Fig. 4.30a

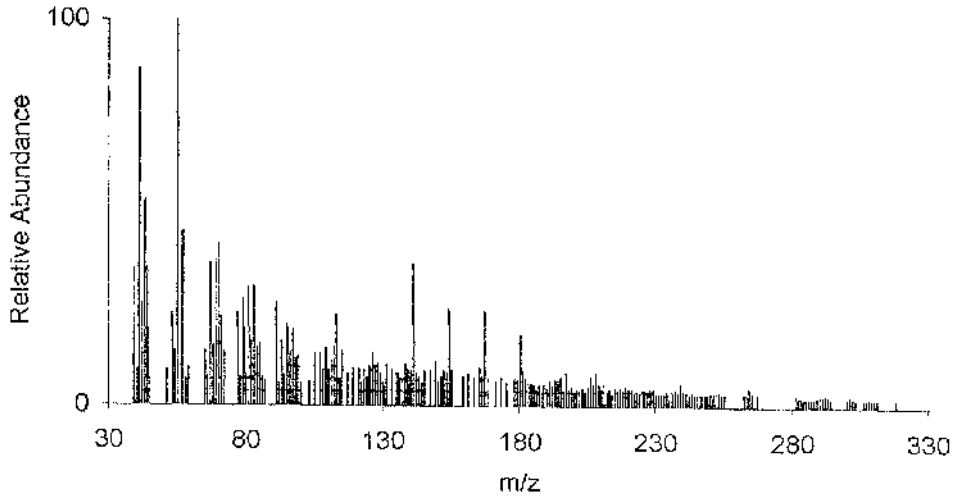
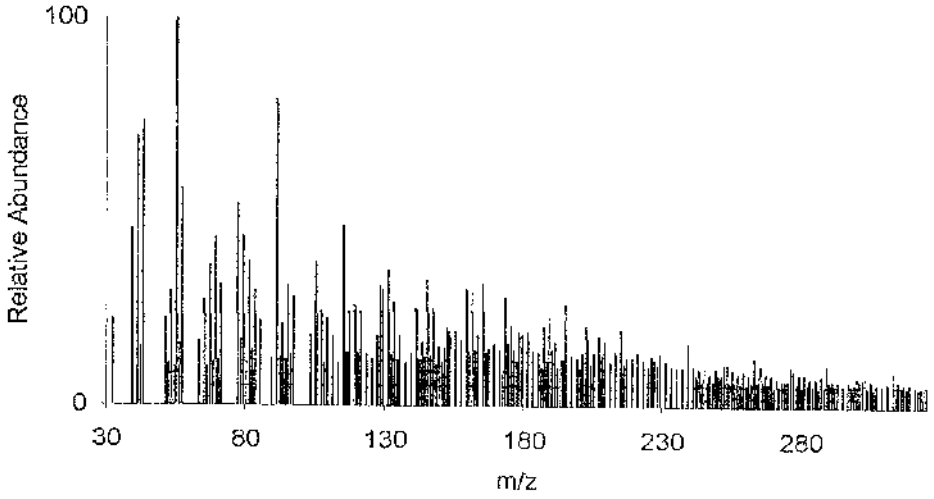


Fig. 4.30b



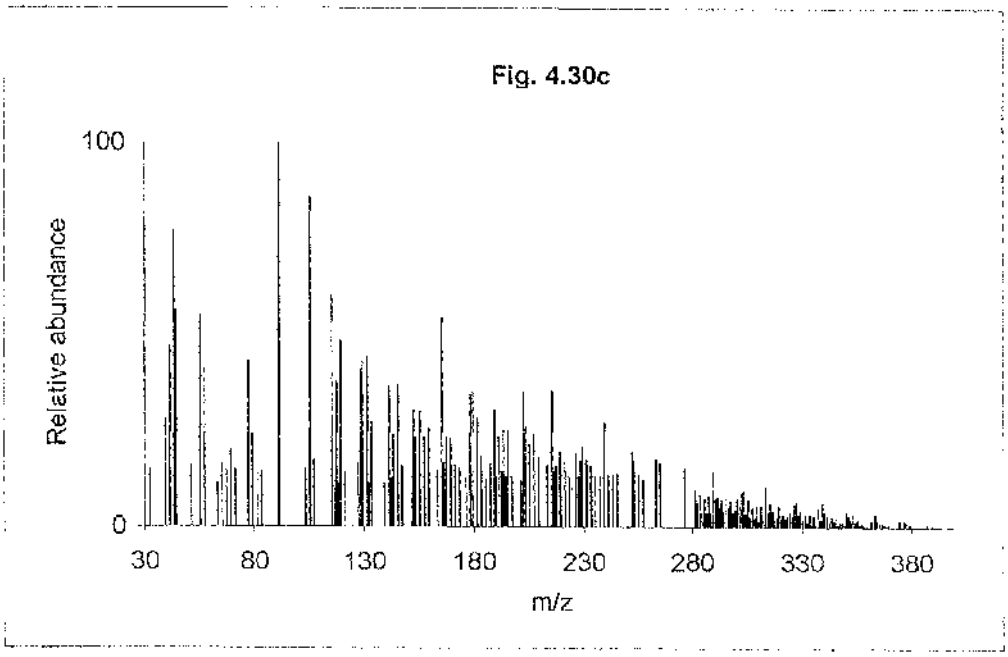


Fig. 4.30 a,b&c Mass spectra of cold ring fraction products of degradation, obtained by heating to 500°C under TVA conditions, of nickel polyacrylate (Fig. 4.30a), copper polyacrylate (Fig. 4.30b) and copper polyacrylate* (Fig. 4.30c).

* made by neutralisation of poly(acrylic acid)

Gaseous Products (identified by FT-IR/Mass Spec.)		Liquid Products (Identified by GC/MS)	
non-condensable at -196°C	condensable at -196°C		
carbon-monoxide hydrogen	ethene propene ketene carbon dioxide acrolein acetone acetylene benzene	toluene 2-cyclopentenone acrylic acid xylenes 2-methylcyclo-pentanone styrene 2-methylcyclo-pent-2-enone 2,3 dimethylcyclo-pent-2-enone benzaldehyde propylbenzene ethyltoluene	3-methylcyclo-hex-2-enone benzofuran trimethylbenzene phenol propenylbenzene methylstyrene propynylbenzene 1-phenyl-1-propanone tolualdehyde o,m-cresol naphthalene

Table 4.5 Volatile products of degradation of zinc polyacrylate.

Gaseous Products (identified by FT-IR/MS)		Liquid Products (identified by GC/MS)	
non condensable at -196°C	condensable at -196°C		
carbon-monoxide hydrogen	ethene propene ketene carbon dioxide acetone	toluene ethylbenzene xylenes styrene propylbenzene cumene ethyltoluene α-methylstyrene	indene cresol 7-methyl-benzofuran 2-methyl-benzofuran naphthalene

Table 4.6 Volatile products of degradation of zinc polyacrylate*.

* made by neutralisation

Gaseous Products (identified by FT-IR/Mass Spec.)		Liquid Products (Identified by GC/MS)	
non-condensable at -196°C	condensable at -196°C		
carbon-monoxide	ethene	toluene	propenyl-benzene
hydrogen	propene	ethylbenzene	o-cresol
methane	ketene	xylenes	1-phenyl-1-propane
	carbon dioxide	styrene	7-methyl-benzofuran
	methanol	propylbenzene	2-methyl-benzofuran
	acetylene	ethyltoluene	
		phenol	
		cumene	
		methylstyrene	

Table 4.7 Volatile products of degradation of cobalt polyacrylate.

Gaseous Products (identified by FT-IR/Mass Spec.)		Liquid Products (Identified by GC/MS)	
non-condensable at -196°C	condensable at -196°C		
carbon monoxide	ethene	toluene	propynyl-benzene
hydrogen	propene	acrylic acid	phenol
methane	ketene	ethylbenzene	cresols
	carbon dioxide	xylenes	1-methyl-1H-indene
	acetone	styrene	2-methyl-benzofuran
	acetylene	propylbenzene	naphthalene
		ethyltoluene	
		2-propenyl-benzene	

Table 4.8 Volatile products of degradation of cobalt polyacrylate*

*made by neutralisation.

Gaseous Products (identified by FT-IR/MS)		Liquid Products (identified by GC/MS)	
non condensable at -196°C	condensable at -196°C		
carbon-monoxide	ethene	benzene	ethyltoluene
hydrogen	propene	acrylic acid	1-propenyl-benzene
methane	carbon dioxide	toluene	phenol
	ketene	ethylbenzene	propynylbenzene
	acetaldehyde	xylenes	butylbenzene
	methanol	styrene	1-methyl-3-propylbenzene
	acetylene	2-propenyl-benzene	p-cresol
		propylbenzene	1-methyl-1H-indene
		benzene	naphthalene
		trimethyl-benzene	

Table 4.9 Volatile products of degradation of nickel polyacrylate.

Gaseous Products (identified by FT-IR/MS)		Liquid Products (identified by GC/MS)	
non condensable at -196°C	condensable at -196°C		
carbon-monoxide	ethene	toluene	propynylbenzene
hydrogen	propene	ethylbenzene	propyltoluene
methane	ketene	xylenes	7-methyl-benzofuran
	carbon dioxide	styrene	2-methyl-benzofuran
	butene	2-propenyl-benzene	3-methyl-1H-indene
	acetaldehyde	propylbenzene	1-methyl-1H-indene
	methanol	cumene	naphthalene
	acetylene	trimethylbenzene	
	benzene	phenol	
		ethyltoluene	
		α-methylstyrene	

Table 4.10 Volatile degradation products of nickel polyacrylate*.

* made by neutralisation

Gaseous Products (identified by FT-IR/Mass Spec.)		Liquid Products (Identified by GC/MS)	
non-condensable at -196°C	condensable at -196°C		
carbon-monoxide hydrogen	ethene ketene propene carbon dioxide acetylene sulphur dioxide acetaldehyde 1,3 pentadiene methanol	toluene acrylic acid ethylbenzene xylenes styrene 2 propenyl benzene propylbenzene trimethyl- benzene phenol	butylbenzene 1-methyl- 3-propylbenzene cresol 2-methyl- benzofuran 1,3 butadienyl- benzene- naphthalene 1-methyl naphthalene

Table 4.11 Volatile degradation products of copper polyacrylate

Gaseous Products (identified by FT-IR/MS)		Liquid Products (identified by GC/MS)	
non condensable at -196°C	condensable at -196°C		
carbon-monoxide hydrogen	ethene propene ketene carbon dioxide	toluene acrylic acid xylenes styrene 2-methylcyclo- pent-2-enone 2,3 dimethyl- cyclopent-2-enone propylbenzene trimethylbenzene 3-methylcyclo-- hex-2-enone (E) propenyl- benzene	2,4,4 trimethyl- 2-butenolide 1-propenyl- benzene indene 1-acetyl- 1-cyclohexene methylpropyl- benzene ethyl-dimethyl benzene cresols 2-methyl- benzofuran

Table 4.12 Volatile products of degradation of copper polyacrylate*

* made by neutralisation

4.6 Discussion

In this section the difference in thermal stability of the polymers obtained by alteration of the metal ion is discussed, as well as the mechanism of polymer degradation with respect to degradation products.

The structure of the transition metal polyacrylates may differ from the essentially electrostatic bonding found in group 1 and 2 polyacrylates and take the form of intra- or intermolecular chelated metal ions, where the metal ion is complexed by two neighbouring carboxylate groups.

Poly(acrylic acid) in solution takes the form of a spherical ball. The addition of metal ions results in repulsive forces which cause the chain to unwind and expand.

Fields & Neilsen[62] said that zinc polyacrylate could have three possible structures. These were an intramolecular salt, an intermolecular salt or a pendant half salt with water. The formation of eight member chelates is rare but evidence of them has been found in copper polyacrylate.

It is expected that differences will exist in the structures of the polymers made by polymerisation of metal acrylate monomer and those made by neutralisation of poly(acrylic acid). The former contains unreacted vinyl groups and the latter unreacted carboxylic acid groups.

Wall and Drenan[63] found that different amounts of Ba^{2+}, Sr^{2+} and Ca^{2+} ions were needed to produce gelation of poly(acrylic acid). They found Ba^{2+} to be the most efficient at gelation, with the cations following the sequence Ba>Sr>Ca. From the large differences in gelation efficiency, they

concluded that cation size was not the only factor involved in gelation and the forces found in the $COO^- M^{2+} {}^-OOC$ bonds were not entirely coulombic.

The essentially electrostatic binding character found in alkaline earth polyacrylates was shown to be different if they were replaced by copper ions. A number of studies have found that copper ions form complexes with the carboxylate groups of poly(acrylic acid) and poly(methacrylic acid).[64-66] Discussion has taken place about whether complex formation consists of two or four co-ordinated carboxylate groups, with two intramolecular carboxylate groups being favoured.

Gregor[67] et al found poly(acrylic acid) has a much stronger preference for ring formation than its monomeric equivalent glutaric acid, and is much closer in its chelating behaviour to smaller dibasic acids like oxalic acid and malonic acid.

Wall and Gill[65] said that initially intramolecular complex formation occurred because the equilibrium constant for the reaction,

$$Cu^{2+} + (COOH)_2 \longleftrightarrow (COO)_2Cu + 2H^+$$

$$K = \frac{[(COO)_2Cu][H^+]^2}{[Cu^{2+}][(COOH)_2]}$$

is found to vary inversely with the first power of the acid concentration and not the square.

Wall and Gill also found that other ions such as nickel, cobalt and zinc exhibit to a small extent, tendencies to form complexes with PAA. Leyte and Mandel[64] said that these ions are bound less strongly to poly(methacrylic

acid) than Cu(II), the order of binding strength being Co(II)< Ni(II)<Cu(II)>Zn(II).

The insolubility of the polymers suggest that intermolecular forces, between separate chains must be present. Due to the divalency of the metal ions each is bonded to two acrylic acid units. During polymerisation it would be expected that some crosslinking by metal ions would occur, as is seen in polymerisations involving other di-vinyl monomers such as di-vinyl benzene. The infra-red spectra of the polymers show a weak absorption due carbon-carbon double bond stretching, less than would be expected if only one acrylic acid group in each monomer unit reacted.

As the polyacrylates made by neutralisation of poly(acrylic acid) are also insoluble there must be ionic intermolecular forces caused either by secondary forces between chelated metal ions of one chain with other chains, or by metal ions acting as crosslinking bridges between chains. During preparation of these polymers early precipitation would be expected if bridging structures were formed. Precipitation occurred after more than 50% neutralisation suggesting that direct metal bridged bonds between separate polymer chains are less prevalent than intramolecular bonding. It is probable that the extent of metal bridge crosslinking is dependent on polymeric acid concentration in the reaction mixture.

4.6.1 Mechanism of Degradation

The volatile degradation products, which are similar for all the transition metal polyacrylates, are similar to those of the alkali and alkaline metal polyacrylates, but smaller numbers of carbonyl-containing residues were identified. The products suggest the mechanism of the breakdown of the polymers involves radical intermediates, which with subsequent bond scissions, rearrangements and hydrogen atom abstractions will form the degradation products identified in section 4.5.

The initial step in the decomposition of the polymers may occur by either of two different processes, both of which lead to the formation of carbon dioxide, the largest single degradation product, and radical intermediate species from which the final products are formed.

The first mechanism shown diagrammatically in **Fig. 4.31** involves main chain scission in the polymer (A) at or near the side groups resulting in intermediate structures (B) and (C). This is followed by side group scission, with elimination of metal carbonate, to form the radical intermediates (D) to (G). Metal carbonate will then undergo decomposition to metal oxide and carbon dioxide. The subsequent reduction of the metal oxide by carbon present in the residue or by carbon monoxide, a degradation product, was observed for zinc oxide and occasionally for copper oxide.

No metal carbonate was found in the residue because at 500°C any carbonates formed with these four metals would decompose to metal oxide and carbon dioxide. In previous studies involving the magnesium and calcium salts metal carbonate was found in the degradation residue, the amount dependent on its thermal stability.

An alternative mechanism for the initial degradation step is described in **Fig. 4.32**. The same radical intermediates will be obtained, if the first step in decomposition is side group scission, again with the loss of metal carbonate, resulting in structure (H). Main chain scission of (H) will give structure (D) and side group scission of (C) leads to (E), (F) and (G), by the same mechanism as found in **Fig. 4.31**.

The radical intermediates formed by the main chain and/or side group scission reactions shown in **Figs. 4.31** and **4.32** can undergo the various

transformations to form the final products of degradation. These mechanisms (**Fig. 4.33**) take into account the formation of the small molecule products identified. Scission from the polymer chain and ring opening of (D), followed by hydrogen atom abstraction can result in the formation of propene, ketene, ethene, acetaldehyde and carbon monoxide. In structure (E), scission from the polymer chain, ring opening and hydrogen atom abstraction will lead to the formation of acetone. Main chain scission of (G) followed by hydrogen atom abstraction results in the structures based on the cyclopentanone ring.

The small amount of products obtained by these mechanisms is probably due to the highly ionic nature of the polymers. The divalent metal ions result in rigid structures inhibiting transfer reactions and favouring the loss of small simple molecules such as hydrogen and carbon monoxide to leave large amounts of a carbon char. The rate of diffusion of degradation products out of the polymer may also be inhibited, resulting in secondary degradation reactions of these products.

Aromatic compounds, containing up to 10 carbon atoms, were obtained as degradation products. Metal carbonate lost by side group scission and the evolution of carbon monoxide and hydrogen as the major non-condensable gases would result in unsaturation in the chain.

Chain scission and folding after the complete loss of side groups would result in the oxygen free aromatics, while the formation of benzofurans and phenolic compounds occur by the incorporation of carbonyl groups that have remained joined to the polymer backbone.

The weight losses observed in thermogravimetry after 500°C and the continual evolution of volatiles in TVA indicate that further breakdown of the residue occurs. This will include the further breaking up of any chain

fragments left after the main chain scissions and any remaining carboxylate ions identified in the residues.

A side group reaction involving the elimination of metal oxide, to form acid anhydride rings, by a non radical process can be discounted. If this were to happen anhydride groups similar to those found in the degradation of poly(acrylic acid) would be expected in the cold ring fraction.

The only only cold ring fraction which contained anhydride type structures was that of copper polyacrylate.* Because of the low metal content in this polymer, the first stage of degradation involved intramolecular dehydration of neighbouring carboxylic acid groups to form anhydride rings.

No monomer was found in the degradation products, as depolymerisation found in polymethacrylates is extremely limited in polyacrylates. If any monomer had formed, it would have be too involatile to distil out of the hot zone, and would have itself degraded.

The most thermally stable of the four metal carbonates is nickel carbonate. Partial degradation, by heating nickel polyacrylate to 320°C did not result in nickel carbonate being identified in the residue.

The shoulder seen in the TVA analysis of cobalt polyacrylate* is thought to be due to the degradation of unreacted carboxylic acid groups found in these polymers. This did not occur to the same extent in the nickel or zinc polymers where the main degradation peaks contained only very small shoulders. The number of unreacted carboxylic acid groups was difficult to determine because it was difficult to ascertain the exact amount of moisture present in these samples and hence the correct metal content.

It may be that in the cobalt polymer stronger ionic forces are present in these polymers. These may produce gelation from solution quicker than for the zinc and nickel polymers resulting in greater numbers of unreacted carboxylic acid groups.

The DTA curves of both nickel polymers and cobalt polyacrylate consist of a large peak followed by a smaller second peak or shoulder. This is not as apparent in the DTG curves where an indistinct shoulder is apparent for both the polymers made by neutralisation but not for the nickel polyacrylate made by polymerisation.

The shoulders may be due to decomposition of carboxylic acid groups or metal carbonate decomposition in the case of the nickel polymers.

The amount of cold ring fraction appears to be related to the stability of the polymers. The zinc and cobalt polymers produce no measurable amount of cold ring fraction, whereas nickel polyacrylate and copper polyacrylate which degrade at lower temperatures do produce cold ring fraction. This like the liquid fraction products maybe due to the greater ionic nature of these salts inhibiting the formation, by intra- or intermolecular transfer reactions of cold ring products or the inhibition of their diffusion through the polymer matrix causing decomposition to secondary products.

The degradation of the two copper polyacrylates follows a more complex pathway. The way in which these two polymers degrade is discussed with respect to the residue and degradation products obtained for each step of the degradation process.

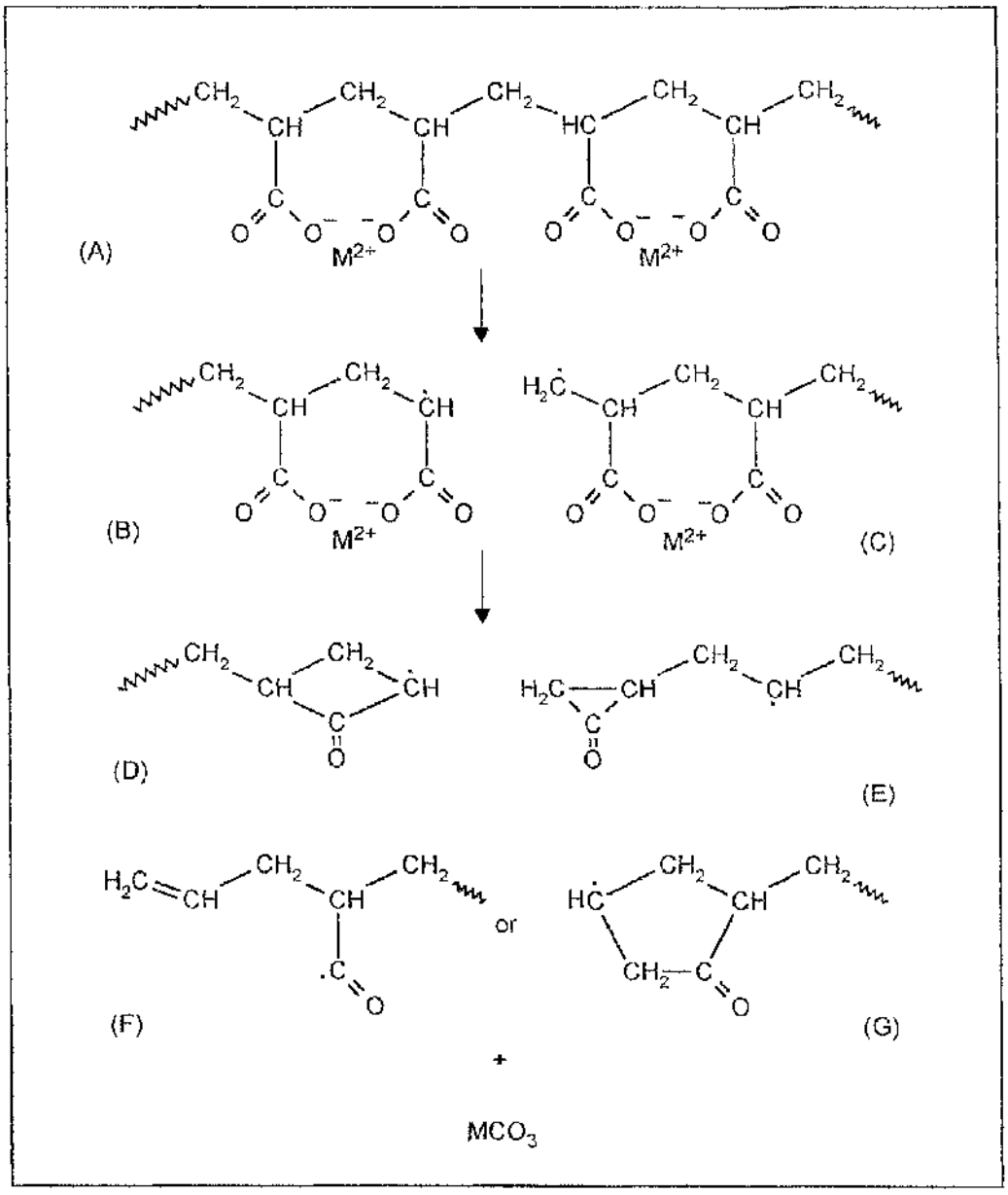


Fig. 4.31 Degradation mechanism of metal polyacrylates.

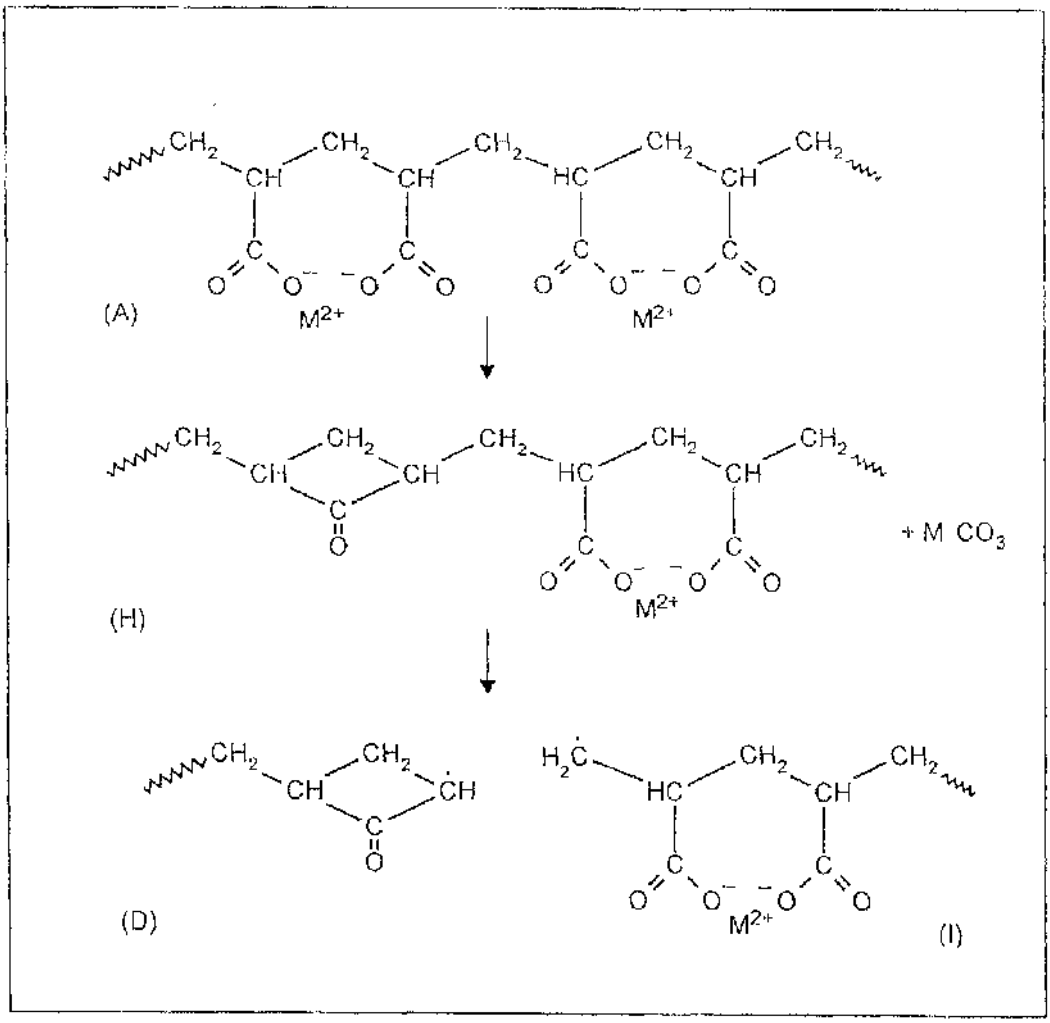


Fig. 4.32 Polymer degradation by side group scission followed by main chain scission.

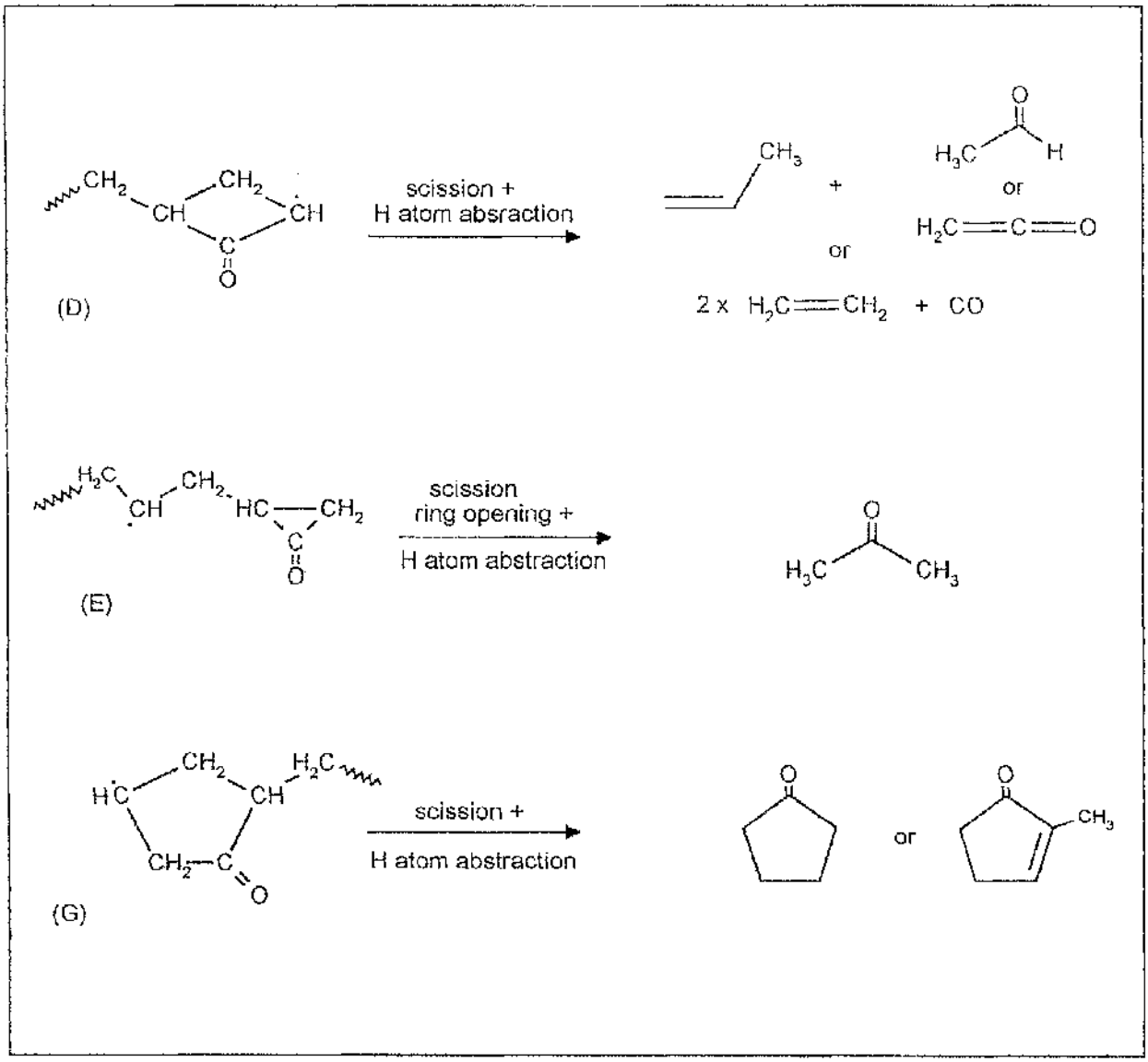


Fig. 4.33 Formation of final degradation products from radical intermediates.

4.6.2 Degradation of Copper Polyacrylate

The first stage in the degradation of copper polyacrylate* up to 265°C is anhydride ring formation by reaction of adjacent carboxylic acid groups. From the low metal content of the polymer, section 3.5.3, it can be said that approximately 35% of carboxylic acid groups remain unreacted in the polymer.

The change in polymer structure is seen in the infra-red spectrum in **Fig. 4.34**. Two bands appear at 1803 cm^{-1} and 1758 $cm,^{-1}$ due to acid anhydride carbonyl absorptions, replacing the carboxylic acid carbonyl stretch at 1713 $cm.^{-1}$ Evidence for the reaction of neighbouring acid groups on the chain, as opposed to intermolecular reactions, is the greater intensity of the lower frequency band at 1758 $cm,^{-1}$ indicative of cyclic anhydrides.

The main absorption for the anti-symmetrical carboxylate absorption in copper polyacrylate* (**Fig. 3.5d**) is found at 1616 $cm,^{-1}$ with a shoulder at 1556$cm.^{-1}$ The absorption at 1616 cm^{-1} is characteristic of bridging carboxylate structures, while the absorption at 1556 cm^{-1} is characteristic of metal ion chelates.[68] A larger absorption at 1552 cm^{-1} replaces the bridging absorption of 1616 cm^{-1} after the first stage of degradation. The bridging carboxylates which predominated in the polymer have been replaced by chelating carboxylates (**Fig 4.34a**).

The main process occurring in the second stage of degradation between 265°C and 370°C is the decomposition of the metal carboxylate groups. After the second stage of degradation the infra-red spectrum of the residue no longer exhibits the absorptions due to the carboxylate absorptions at 1552 cm^{-1} and 1412 $cm.^{-1}$ The shape of the infra-red spectrum (**Fig. 4.34b**) is also in agreement with the formation of copper oxide at this temperature.

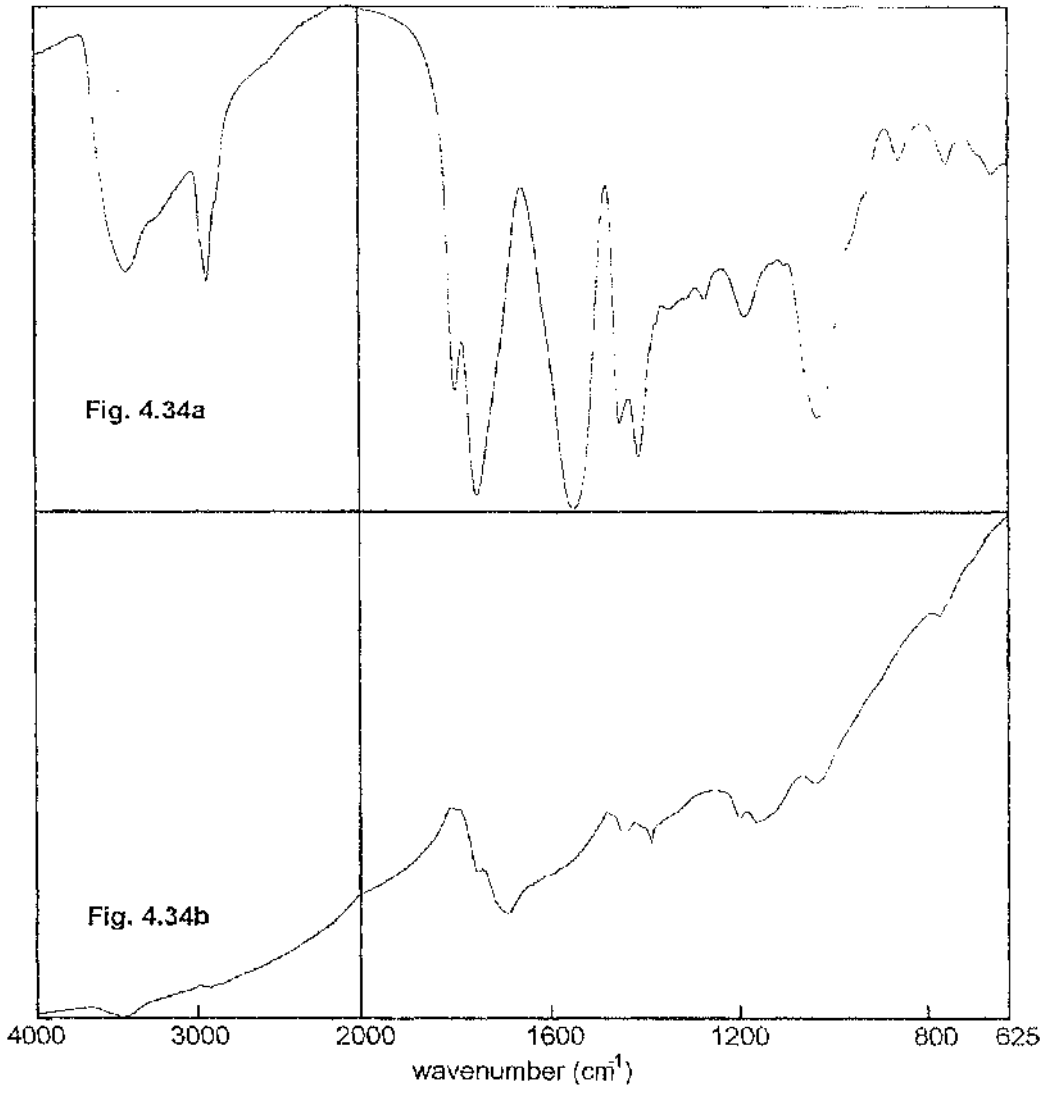


Fig. 4.34a Infra-red spectrum of the residue of copper polyacrylate, after heating to 265°C, under TVA conditions.

Fig. 4.34b Infra-red spectrum of the residue of copper polyacrylate, after heating to 370°C, under TVA conditions.

A comparison of the residues obtained at 265°C and 370°C (**Fig. 4.35**) shows the anhydride structures in both spectra and the appearance of a broad absorption at 1700 $cm_{,}^{-1}$ due to carboxylic acid groups. These two type of products are obtained in the cold ring fraction at 500°C. It can also be seen that the carboxylate stretching bands at 1410 cm^{-1} and 1550 cm^{-1} have disappeared.

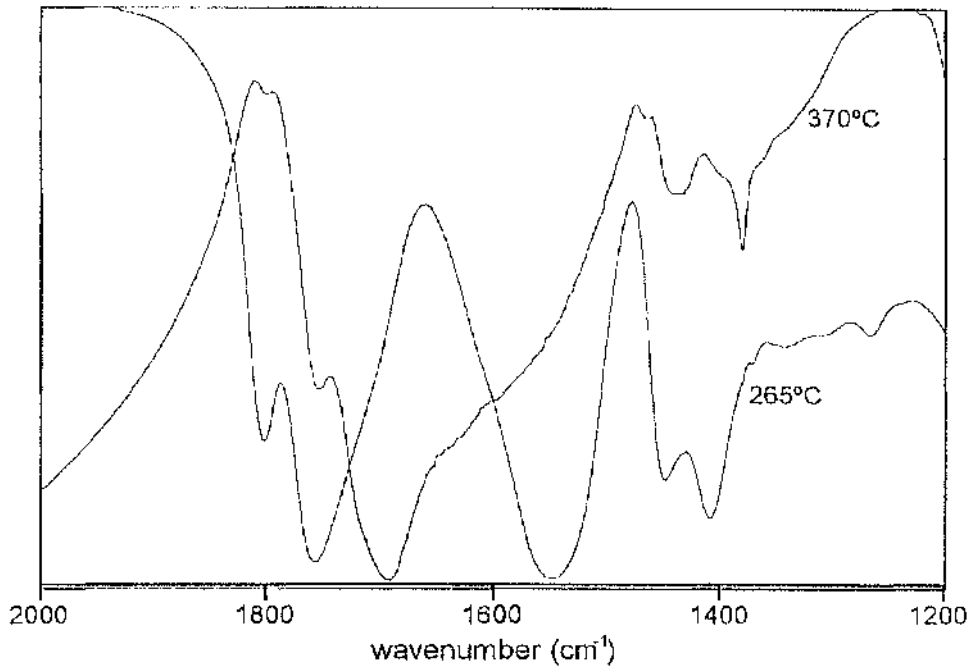


Fig 4.35 Infra-red spectra of copper polyacrylate after heating to 265°C and 370°C, under TVA conditions.

One of the products obtained from the second stage of degradation was propene. This together with the infra-red spectrum of the residue would infer that main chain scission has occurred during the degradation of the carboxylate groups, but chain fragments containing carboxylic acid and anhydride structures remain.

The final stage of degradation consists of the further break up of chain fragments to form the alkyl aromatic and oxygen-containing aromatic

compounds, found by GC-MS analysis (section 4.5.5). The decomposition of anhydride and acid groups and the formation of small fragments containing these groups, that are found in the cold ring fraction, will also occur.

The residue after the final stage of degradation is discussed in section 4.5.2.

Detailed observation of the different stages of degradation of copper polyacrylate was made more difficult because the extreme reluctance of copper acrylate to polymerise resulted in only a small amount of sample being available.

The infra-red spectrum of copper polyacrylate has an absorption at 1637 $cm.^{-1}$ After the first stage of degradation at 256°C the change in the infra-red spectrum is the disappearance of the small shoulder at 1637 $cm.^{-1}$ The disappearance of this band would indicate the decomposition of the remaining pendant vinyl groups

The main degradation step of the copper carboxylate groups occurs between 256°C and 330°C which is a similar range to the polymer made by neutralisation of poly(acrylic acid). No anhydride structures are found in this residue and none were found in the cold ring fraction, but the carboxylic acid absorptions were observed.

The final stage of degradation between 330°C and the end of heating consists of the break up of the remaining polymer chains to form the cold ring and other products identified by GC-MS.

It is possible that the final two peaks seen in the copper polymers, where the first is due to metal carboxylate decomposition and the second to

further chain scission merge in the nickel and cobalt polyacrylates. As the thermal stability of the metal carboxylate bond increases in the zinc polyacrylates they combine into a single peak, caused by both metal carboxylate and polymer chain decomposition.

4.6.3 Effect of Metal Ion on Thermal Stability of Polymers

Unlike alkali and alkaline earth metal polyacrylates which do not show any significant change in the degradation temperature with variation in the metal ion, the degradation temperature of the transition metal polyacrylates was greatly influenced by the choice of metal.

Irving and Williams[69] found that the stability of complexes formed by bivalent ions of the first transition series followed the sequence Co<Ni<Cu>Zn and was irrespective of the number or nature of the ligands involved.

This is the complete opposite to the results obtained for the thermal stability in this experiment for polyacrylates and also for polymethacrylates,[60] succinates,[70] acetates[71] and formates[72] where the stability sequences are similar. These results follow the stability sequence Zn≈Co>Ni>Cu.

A number of factors will influence the thermal stability with respect to the metals. Also, It must be taken into account that zinc is not considered to be a transition metal as it has a full 3d electron shell. Comparing the stability of the transition metals separately may therefore have some merit.

From the graphs in **Fig. 4.36** it can be seen that some trends in the characteristics of the metal ions can be compared with the thermal

stability of the polyacrylates while others appear to bear no relation (**Fig.4.36d**), but these are only empirical observations.

The thermal stability sequence follows a trend across the first transition sequence, where a decrease in thermal stability occurs with an increase in atomic number (**Fig 4.36a**). There is an increase in the number of electrons in the 3d shell and also effective nuclear charge until zinc, which has a full $3d^{10}$ shell, possibly an important factor in its stability.

If the cations present are considered as elementary catalysts of the thermal degradation process, their catalytic efficiencies can be related to heat of cation formation, i.e. catalytic efficiency increases with increasing ionisation enthalpy. The ionisation enthalpies (**Fig. 4.36b**). show an increase for the cobalt, nickel and copper sequence which is the opposite of the thermal stability sequence, i.e. a decrease in thermal stability is seen as the ionisation enthalpy increases, but not for Zn^{2+} which has a heat of formation greater than that of cobalt and nickel.

The thermal stability sequence is also the opposite to the trend in the value of the electronegativities of the metals (**Fig. 4.36c**). The metal polyacrylates with the lower thermal stability have metals which have higher electonegativity values. The difference in ionic radii of the cations is small compared to the difference obtained when descending a particular group in the periodic table and has no direct correlation with thermal stability.

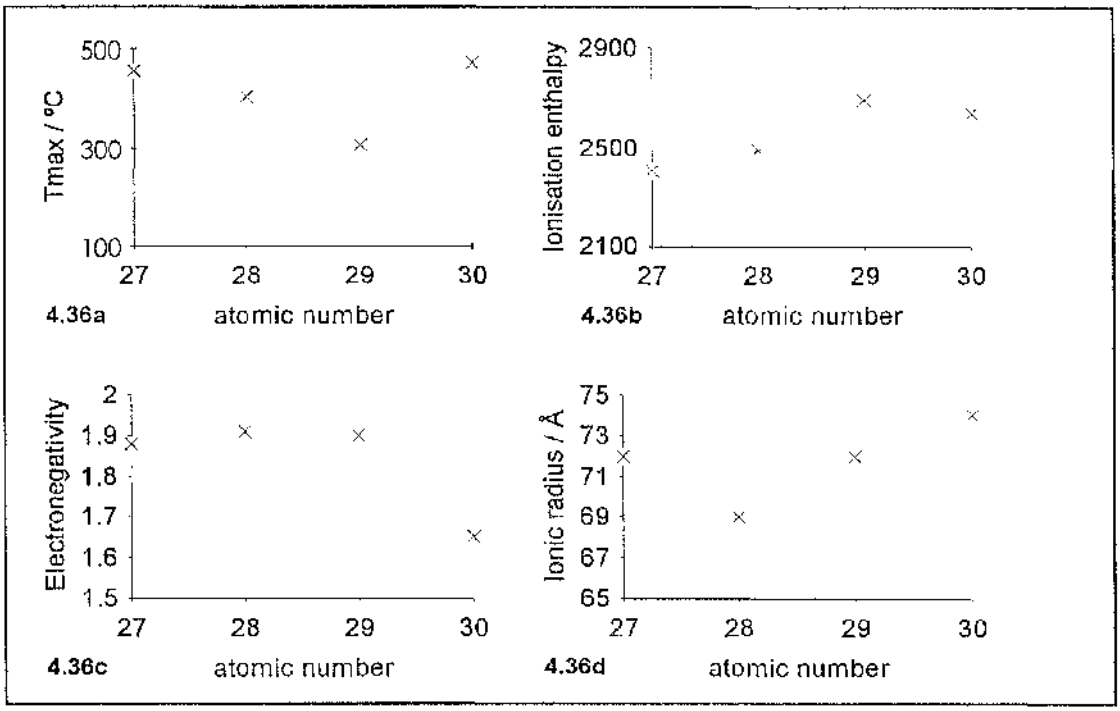


Fig.4.36 Trend of metal properties versus atomic number

The polymers differ from simple metal ligand complexes in that the best conformation required for metal-polymer chain bonding must take into account strain produced in the polymer backbone and electrostatic repulsion between carboxylate groups. Mutual compatibility is required between the geometry of the polymer chain and the stereochemistry favoured by the cation if maximum stability is to be attained.

The reason for the poorer stability of the copper salts is not clear, but this also seen for other copper carboxylates. A possible explanation is the greater stability and binding strength found for copper complexes compared to the other metals.

Wall[65] found that with poly(acrylic acid) intramolecular association through copper ions occurs to such an extent causing partial constriction of the chains opposed by the increasing ionic charge. He found that other ions like those of cobalt, nickel and zinc exhibit the tendency to form

complexes with poly(acrylic acid) to a smaller extent than copper. Leyte[64] found that substitution of alkaline earth ions with copper ions in salts of poly(methacrylic acid) results in a different kind of binding from the essentially electrostatic forces. He found evidence for the formation of complex structures which appear to involve carboxyl groups associated with copper ions. The strong forces between copper ions and carboxylate ligands in these complexes may produce greater strain by increasing the rigidity of the polymer chains, relative to the forces produced by weaker complexation found with other metals.

The constriction in the polymer chains due to ionic bonding will also be opposed by the increasing net ionic charge that attends increasing neutralisation. This may account for the thermal stability sequence being the opposite to that found for the order of binding strength and effective nuclear charge.

A decrease in thermal stability does occur as the atomic number of the transition metals increases,but the zinc polymers do not continue this trend. It is probable that a combination of a number of different and complex factors contribute to the overall stability of the polymers thereby making it impossible to say exactly why they follow the stability sequence found in this study. The difference in thermal stability of the zinc polymers may be due to the non transition metal characteristics of zinc.

CHAPTER FIVE

THERMAL DEGRADATION OF COPOLYMERS OF STYRENE AND ACRYLIC ACID

5.1 INTRODUCTION

In this chapter the thermal stability and degradation of copolymers of styrene with acrylic acid and the zinc salts of these copolymers is discussed.

Polystyrene is a linear polymer which is chemically inert and quite resistant to alkalis, acids and reducing agents. It is easy to process, with good stability and flow for injection moulding. It is readily attacked by solvents, has poor outdoor stability and is brittle with a low heat deflection temperature. Many of the deficiencies have been overcome by the use of additives, by copolymerisation or blending.

The thermal degradation of polystyrene has been the subject of many studies and there has been much discussion about the mechanism of decomposition.[73-79] Staudinger[80] studied the products of thermal degradation of polystyrene in his attempts to prove the linear nature of polymers. The initial decrease in molecular weight, below 300°C, is thought to be due to chain homolysis and disproportionation with no volatile substances evolved. This is believed to be principally due to weak links, incorporated during polymerisation, caused by the presence of oxygenated structures, head to head arrangements or unsaturation. Above 300°C polystyrene degrades giving styrene, formed by depolymerisation, at

between 40 -60% of the original weight as the main degradation product, along with small amounts of toluene and α–methylstyrene. The other major products are oligomers, ranging from dimer to pentamer in decreasing amounts, formed by mainly intramolecular, with some intermolecular, transfer reactions.

Copolymerisation of styrene with various monomers has been used to enhance the heat and impact resistance of polystyrene without affecting the other desirable properties. Comonomers are used that increase intermolecular forces due to the presence of polar groups or those that stiffen the chain and reduce rotation through steric hindrance. In commercial use a copolymer containing 76% styrene and 24% acrylonitrile has a greater heat deflection temperature and more resilience and impact strength than polystyrene, but is slightly yellow in colour.[91]

The characteristics and behaviour of polymers can be radically altered by the introduction of crosslinks between different polymer chains. Crosslinked polymers tend to be more stable to heat, insoluble and cannot be made to flow or melt. Mechanical properties such as tensile strength and stiffness may also be improved.

The alteration of polymers by crosslinking is a well established process. The crosslinks can be introduced by a number of methods either during or after polymerisation or in the case of thermosetting resins simultaneously with the last stages of polymerisation.

Crosslinking reactions that occur during chain polymerisations are achieved by the introduction of small amounts of divinyl monomer into the reaction mixture. The number of crosslinks formed during a polymerisation can be controlled by the amount of divinyl monomer used.

Crosslinking after polymerisation can be achieved by using divinyl monomers where the reactivity of one vinyl group is reduced to prevent it entering the polymerisation reaction under the same conditions as the other but can be made to react later under more vigorous conditions.

Radiation crosslinking caused by the interaction of polymers with high energy radiation which results in bond scission to form radicals or unsaturated structures in the polymers chains which react to form crosslinks. This has been found to have beneficial effects on the mechanical properties of some polymers and is used commercially to produce polyethylene with enhanced stability and resistance to flow.

A third method to introduce crosslinks into polymers is by the reaction of groups attached to the polymer chain with crosslinking agents. The most common method is vulcanisation of elastomers with sulphur. This is believed to be principally due to the formation of chemical crosslinks between polymer molecules. Crosslinking can also be achieved by reacting small numbers of carboxylic acid groups on the polymer backbone with metal salts forming metal ion bridges. These crosslinks are labile at processing temperatures allowing moulding or extrusion by conventional methods.

In general use the term Ionomer describes polymers consisting of a hydrocarbon backbone containing pendant acid groups partially or completely neutralised to form salts.[4] The ionic groups can be introduced into the backbone by copolymerisation with acrylic or methacrylic acid or by modification of existing polymers by carboxylation or sulphonation.

The presence of ionic groups can cause significant changes in the viscoelastic, mechanical and optical properties of these polymers.

Much work and discussion has been devoted to the structures of these polymers.[62-67] The changes in the properties of ionomers have been attributed by Eisenberg[82] to the aggregation of ions. The salt groups are thought to occur in two different environments termed multiplets and clusters. Multiplets consist of small numbers of about 6-8 ion dipoles which associate to form higher multipoles dispersed in hydrocarbon matrix and are not phase separated from it .Clusters are microphase separated regions of less than 5 nm rich in ion pairs but also containing quantities of hydrocarbon. The proportion of salt groups which reside in either of the two environments is determined by the nature of the backbone, total concentration of side groups, their distribution along the backbone and their chemical nature.

The tendency of the ionic groups to form clusters has been the source of many investigations into their possible use in improving the compatibility of polymers in blends by introducing small amounts of salt groups.

The compatibility of polystyrene with other polymers in blends has been increased by the addition of acrylic acid salt groups. Vollmert[68,69] found that acrylic acid-styrene and acrylic acid-butylacrylate copolymers were only compatible when the carboxylic acid groups were partially or completely neutralised. He also found the compatibility of the blends to depend on the composition, degree of neutralisation and cation type.

Polystyrene based ionomers can be prepared by either modification of existing polymers by sulphonation of the aromatic ring or by copolymerisation of styrene with acrylic or methacrylic acid monomers.

Styrene-acrylic acid copolymers have found commercial use in adhesives and coatings. The addition of zinc oxide and zinc carbonate to styrene-acrylic acid copolymer based paints has been found to affect the chalking, mould resistance and yellowing of the paints[90].

An increase in the number of acrylic acid units results in a decrease in the thermal stability of styrene-acrylic acid copolymers. Suchoka-Galas[91] found that complete neutralisation of acrylic acid-styrene copolymers as the sodium salt improved their thermal stability and that at similar degrees of neutralisation, stability increased with increasing acrylic acid content. Gronowski[92] found that the thermal stability of zinc acrylate-styrene copolymers increase with increasing metal content, while in the corresponding copolymers containing cobalt, nickel and copper ions the thermal stability decreased with increasing metal content.

Wlochowicz and Eder[93] studied the heat stability of styrene-zinc acrylate copolymers by TG, DTG and DSC with heating rates of 5,10 and 20°C/min. They found the glass transition temperature increased as the amount of zinc acrylate in the polymer increased. Thermogravimetric analysis by heating at 10C°/min was reported to result in a three stage decomposition with the heat stability lowered by increasing the number of ionic groups.

McNeill and Liggat[94] studied the thermal degradation of various copolymers of styrene with methacrylic acid. They found the copolymers to be intermediate in stability between polystyrene and poly(methacrylic acid). with the degradation products mainly those expected by comparison with those obtained from the homopolymers.

5.2 *THERMOGRAVIMETRIC ANALYSIS*

The thermal degradation of the styrene/acrylic acid copolymers and their zinc salts, whose preparation is described in chapter, was studied by thermogravimetric analysis. The mole percentage composition of acrylic acid in the copolymers 1.7%, 5.8% and 11.8% respectively. Samples of approximately 5 mg in powder form were heated at 10°C/min up to 500°C under a nitrogen flow of 50 ml/min.

The curves obtained for each of the copolymers and their corresponding zinc salts are shown on the same set of axes in **Figs. 5.1** to **5.3**, with the main features listed in **Table 5.1**.

The early weight loss was attributed either to the loss of any solvent retained in the copolymers from their preparation or moisture absorbed during storage. The introduction of polar or ionic groups to the copolymers would increase their hygroscopicity. The ionic clusters found in ionomers are available sites for the absorption of moisture. This agrees with the results for the early weight loss where the copolymer containing 11.8% acrylic acid units and its zinc salt showed the largest loss. The possibility of anhydride ring formation, by loss of water, by the reaction between two acrylic acid units was discounted by heating the copolymer containing 11.8% acrylic acid units to 200°C. Examination of the infra-red spectrum of the copolymer showed no change to the carboxylic acid carbonyl absorption band and no bands appearing due to anhydride group formation.

The copolymers decompose in a single step which accounts for between 87% and 97% of the total polymer weight. No pattern could be ascertained with respect to the amount of residue at 500°C as a function of the number of acrylic acid units in the copolymer, but as expected the zinc salts had a larger residue due in part to the zinc or zinc oxide

remaining in the sample pan. The addition of zinc ions had the effect of raising the onset temperature of the main decomposition step by approximately 10°C for the copolymer containing 1.7% acrylic acid units and up to 20°C for the copolymer with 11.8% acrylic acid units. The rate of weight loss after the onset temperature was also lower for the metal salts than their corresponding copolymer.

As the amount of acrylic acid in the copolymers increased there was a small decrease in the temperature of maximum rate of weight loss. This amounted to 13°C between the polymers with 1.7% and 11.8% acrylic acid units. Comparison of the temperatures of maximum rate of weight loss between each copolymer and its zinc salt shows a small increase in temperature by the addition of the zinc ions of between 4°C, for the 1.7% acrylic acid copolymer and 9°C for the copolymer containing 11.8% acrylic acid units.

The accuracy of measurement of these small temperature differences is greatly dependent on positioning of plotter pen on paper. For the small temperature differences found in the experiments these errors would have to be regarded as significant.

The copolymer containing 1.7% acrylic acid units shows no weight loss up to 325°C, the onset temperature for the main weight loss. This weight loss occurs between 325°C and 450°C and is 98.3% of the original weight of polymer, with the maximum rate of weight loss occurring at 413°C. The residue at 500°C was 1.7% of the total polymer weight.

The zinc salt of the 1.7% acrylic acid/styrene copolymer loses 0.75% of its starting weight up to 332°C, the onset temperature for the main weight loss. The main weight loss between 332°C and 450°C is 87.5% of the total

weight, with the maximum rate of weight loss found at 417°C. The residue at 500°C was 11.75% of the starting weight.

The copolymer containing 5.8% acrylic acid units shows no weight loss up to 290°C, the onset for the main weight loss. Between 290°C and 450°C, 97% of the total weight of polymer is lost. The maximum rate of weight loss is at 406°C. The residue at 500°C is 3% of the original weight.

The zinc salt of the 5.8% acrylic acid/styrene copolymer shows no weight loss up to the onset temperature of degradation at 300°C. The weight loss between 300°C and 450°C is 96.5% of the total weight. The maximum rate of weight loss occurs at 413°C. The residue at 500°C is 3% of the original weight.

The copolymer containing 11.8% acrylic acid units shows a weight loss below 300°C of 1.75%. The onset temperature for the main weight loss occurs at 300°C with 94% of the polymer weight being lost between this temperature and 450°C. The maximum rate of weight loss is at 399°C. The residue at 500°C accounts for 4% of the original weight.

The zinc salt of the 11.8% acrylic acid copolymer loses 2% of its weight below 325°C. The onset temperature for the main weight loss is at 320°C, with 90% of the total weight lost between 320°C and 450°C. The maximum rate of weight loss occurs at 408°C. The residue at 500°C is 8% of the original weight.

5.3 DIFFERENTIAL SCANNING CALORIMETRY

The polymers were also studied by differential scanning calorimetry. Samples of approximately 5 mg in powder form were heated up to 500°C at 10°C/min under a nitrogen flow of 60 ml/min.

The results obtained for the copolymers and their zinc salts are shown on the same diagrams in **Figs. 5.4** to **5.6** with the features listed in **Table 5.1**.

Small endothermic kinks in the curves seen at approximately 125°C are due to the polymers reaching their glass transition temperatures. The T_g values for the copolymers were all at 120°C. For the zinc salts the Tg values increased with an increase in metal content. The zinc salts of the copolymer containing 5.8% and 11.8% acrylic acid units had glass transition temperatures of approximately 131°C and 153°C respectively. The position of the glass transition temperature of the zinc salt of the 1.7% acrylic acid/styrene copolymer was not clear but was estimated to be approximately 2°C higher than for the corresponding polymer. These observations agree with a number of studies[92,93,95] which found the glass transition temperature increased with increasing metal content.

A single endothermic peak due to the decomposition of the polymers is the main feature of the curves. The onset temperature for this peak is from 10-30°C lower for the acid copolymers than for their zinc salts, with the difference greatest for the copolymers with 11.8% acrylic acid. In all three cases the maxima of the curves are approximately 5°C degrees lower for the copolymers than the zinc salts.

The results obtained for the TG and DSC analysis are similar. The difference in temperatures for maximum rate of weight loss and maximum heat flow range from 2-10°C. The larger difference in the onset temperature for the degradation stage may be due in some part to errors in judging from the graphs where these occur.

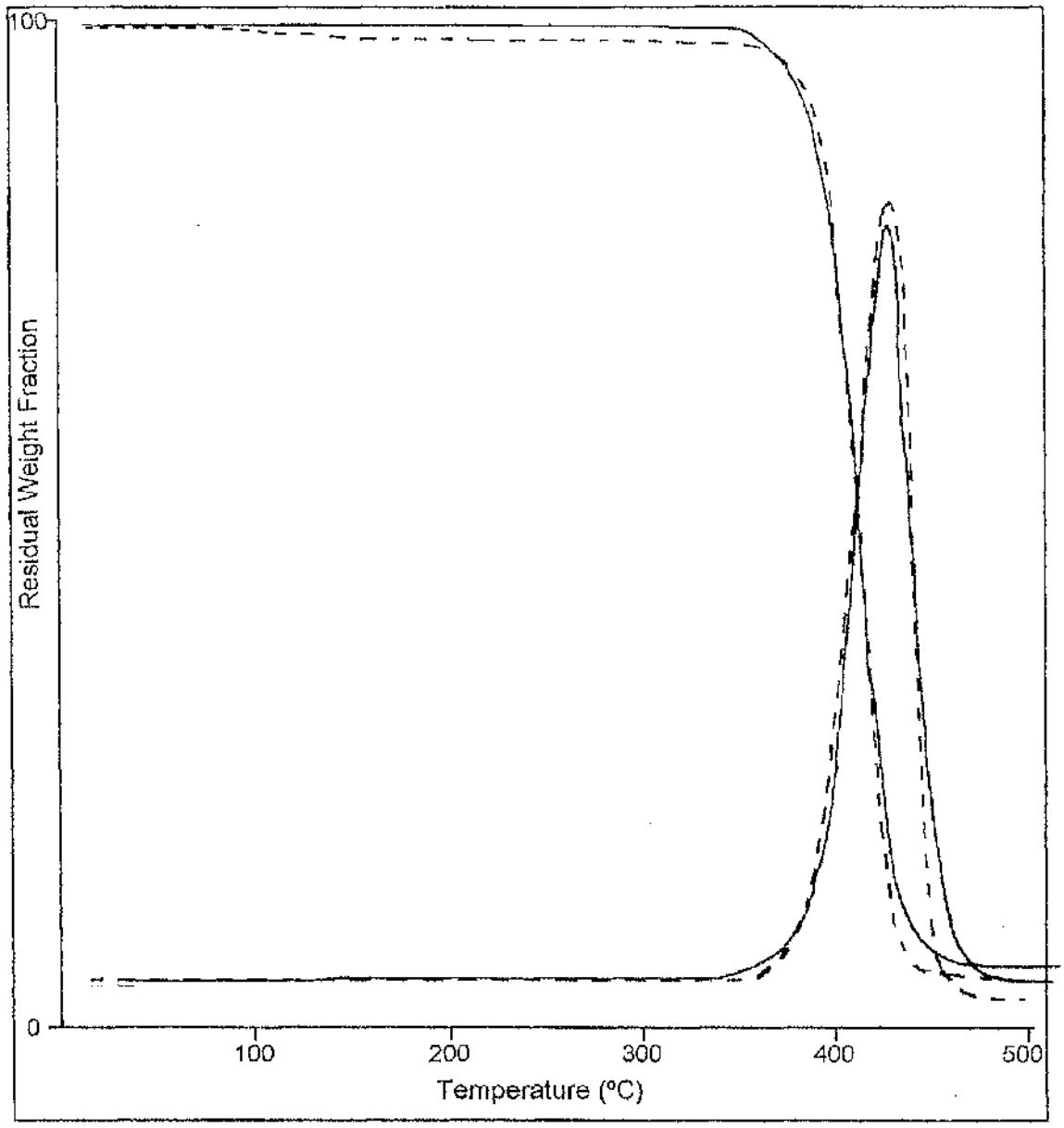


Fig. 5.1 ——— TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the acrylic acid/styrene copolymer, containing 1.7% acrylic acid units.

– – – – – TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the zinc salt of the acrylic acid/styrene copolymer, containing 1.7% acrylic acid units.

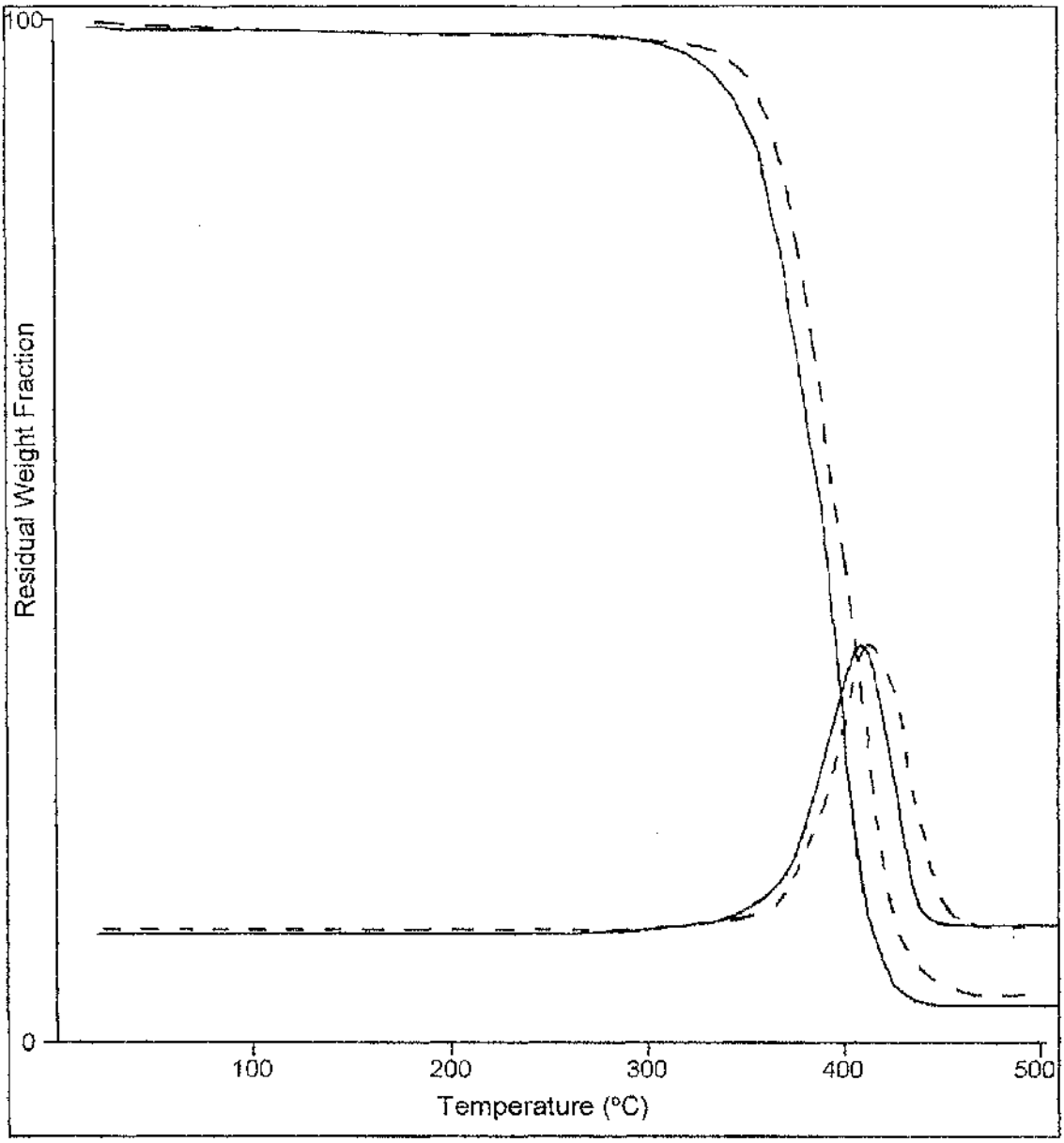


Fig. 5.2 ———— TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the acrylic acid/styrene copolymer, containing 5.8% acrylic acid units.

– – – – – TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the zinc salt of the acrylic acid/styrene copolymer, containing 5.8% acrylic acid units.

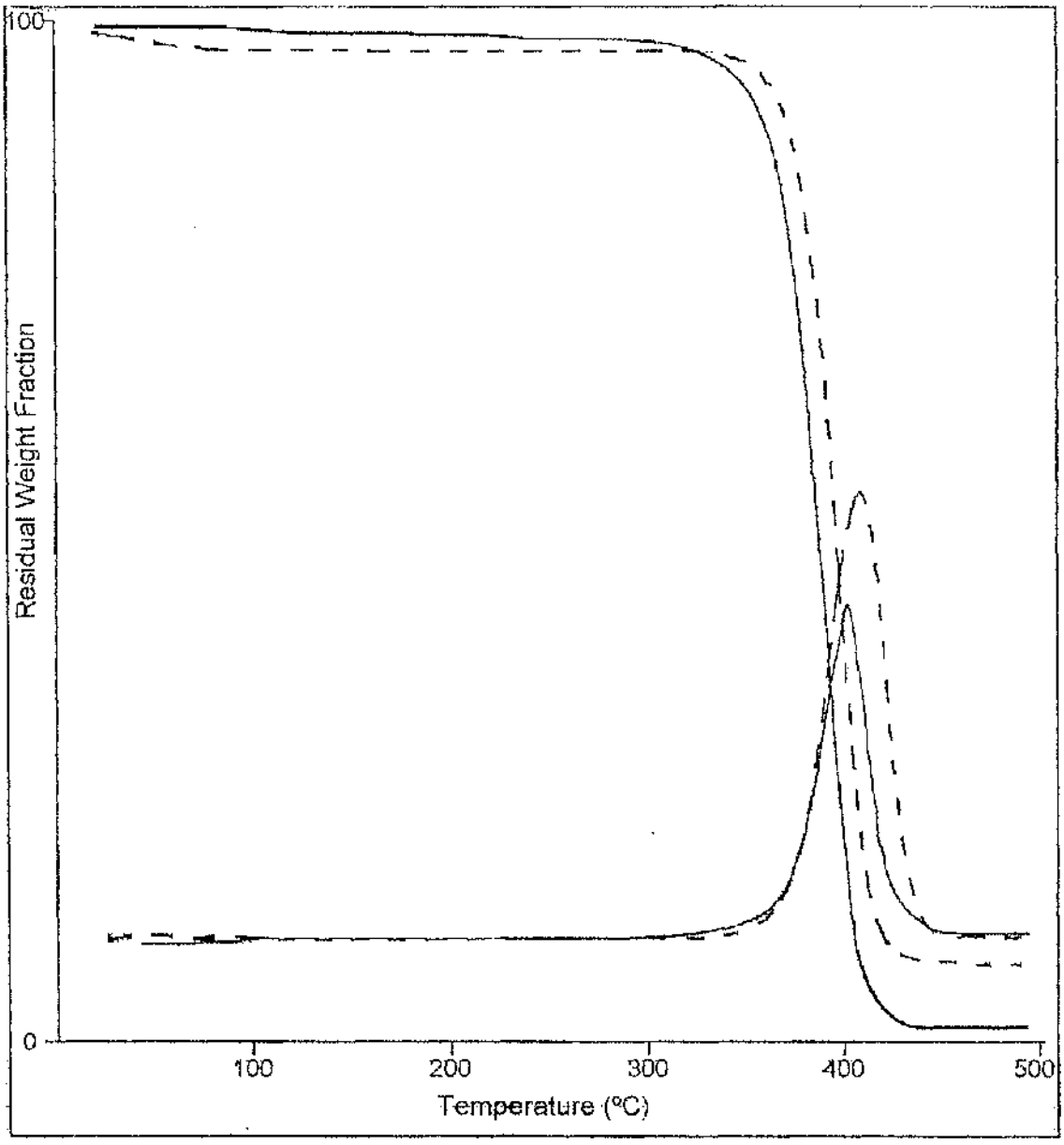


Fig. 5.3 ——— TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the acrylic acid/styrene copolymer, containing 11.8% acrylic acid units.

- - - - - - TG and DTG curves obtained (heating rate 10°C/min, nitrogen flow) for the zinc salt of the acrylic acid/styrene copolymer, containing 11.8% acrylic acid units.

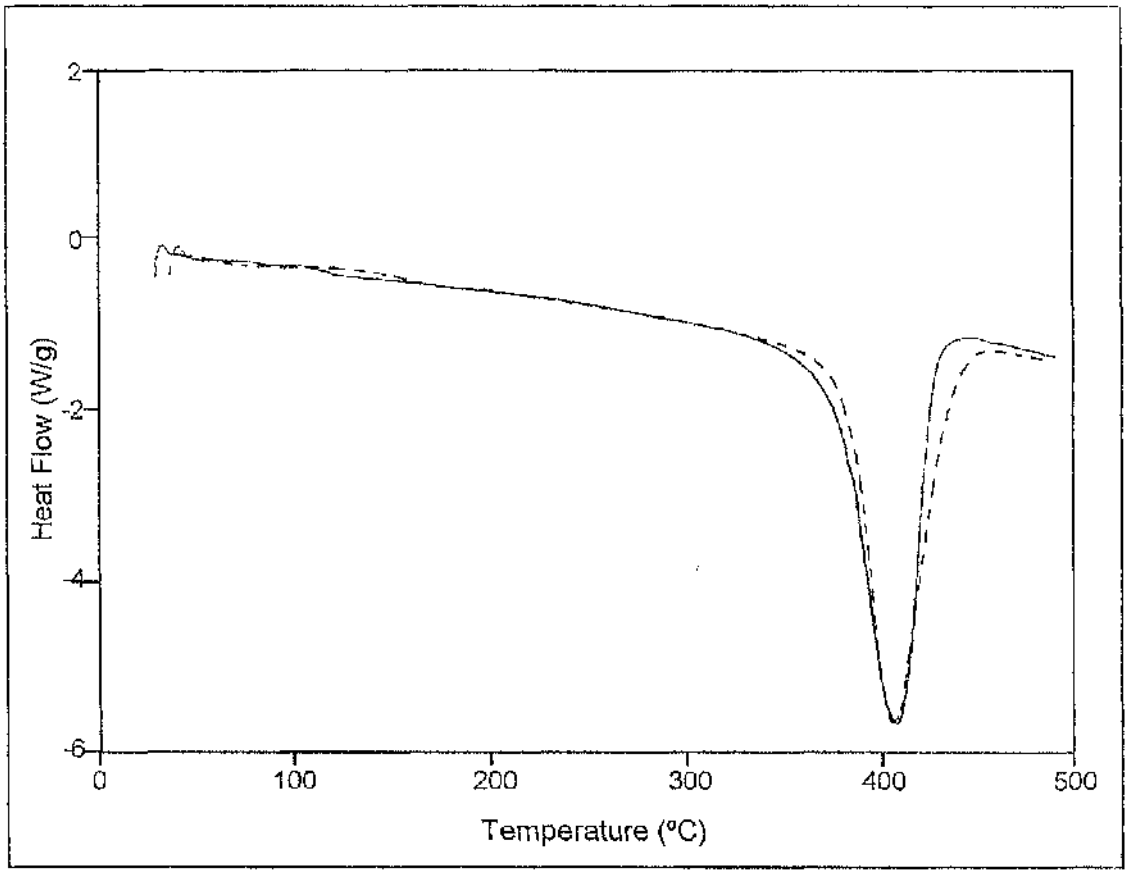


Fig. 5.4 ——— DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the styrene/acrylic acid copolymer, containing 1.7% acrylic acid units.

- - - - - DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the zinc salt of the styrene/acrylic acid copolymer, containing 1.7% acrylic acid units.

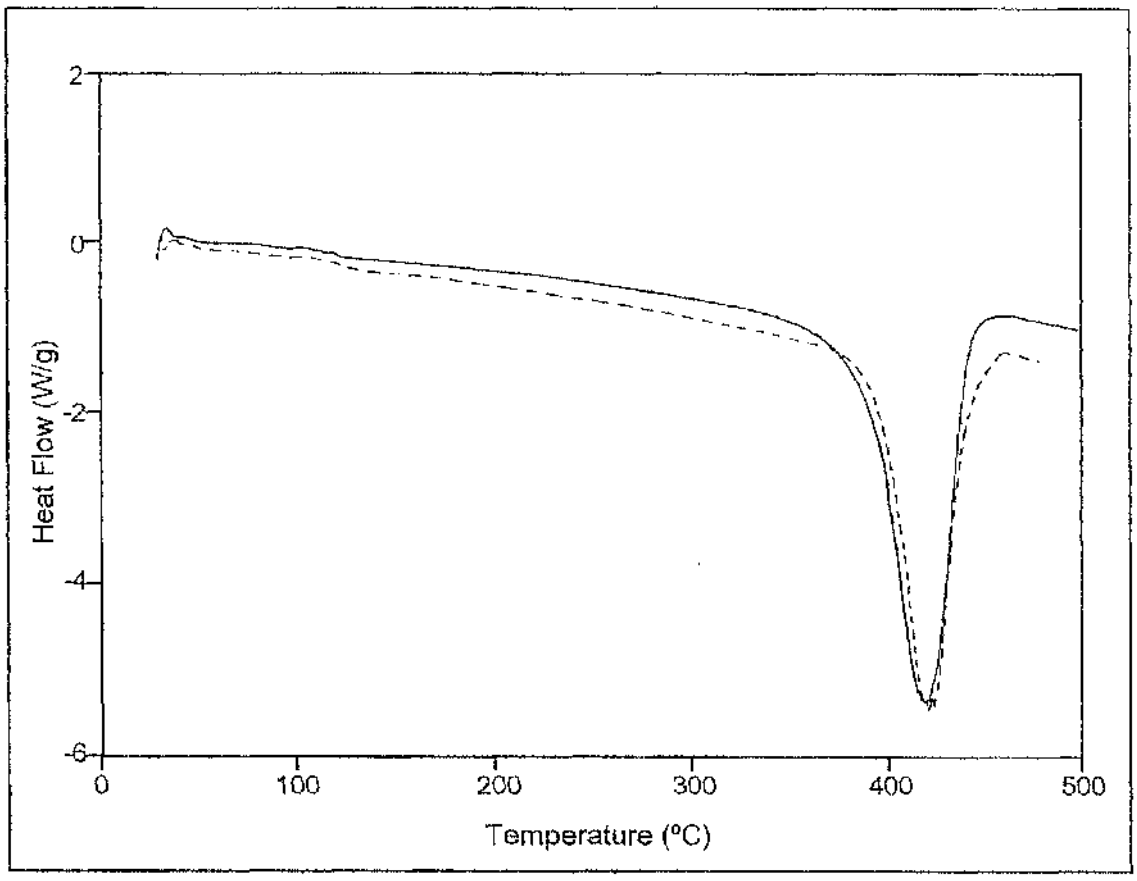


Fig. 5.5 ——— DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the styrene/acrylic acid copolymer, containing 5.8% acrylic acid units.

- - - - - DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the zinc salt of the styrene/acrylic acid copolymer, containing 5.8% acrylic acid units.

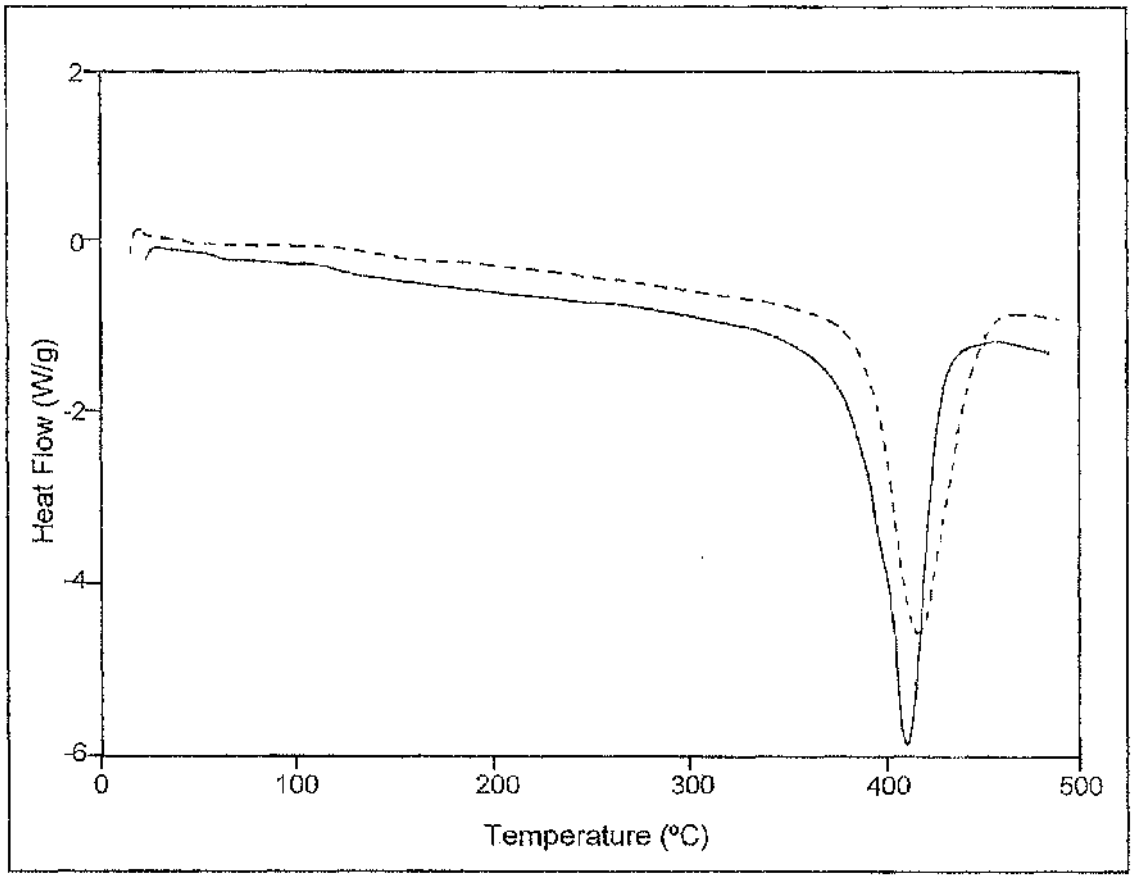


Fig. 5.6 ——— DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the styrene/acrylic acid copolymer, containing 11.8% acrylic acid units.

- - - - - DSC curve (heating rate 10°C/min, nitrogen flow) obtained for the zinc salt of the styrene/acrylic acid copolymer, containing 11.8% acrylic acid units.

	DTG		TG		DSC	
	Peak temp. °C	Temp. range °C	% weight loss for stage	% weight loss to 500°C	Peak temp. °C	Temp. range °C
1.7% AA/St	413	325-450	98.3	98.3	416.5	340-460
1.7% AA/St+Zn^{2+}	417	332-450	86.6	88.3	419.2	350-460
5.8% AA/St	406	290-450	97	97.3	415.8	340-440
5.8% AA/St+Zn^{2+}	413	300-450	96.0	97.0	419.4	355-460
11.8% AA/St	399	300-450	96.0	99.7	410.3	325-460
11.8% AA/St+Zn^{2+}	408	320-450	89.2	92.2	416.1	345-460

Table 5.1 TG, DTG and DTA data for acrylic acid/styrene copolymers

1.7% AA/St	acrylic acid/styrene copolymer containing 1.7% acrylic acid units.
5.8% AA/St	acrylic acid/styrene copolymer containing 5.8% acrylic acid units.
11.8% AA/St	acrylic acid/styrene copolymer containing 11.8% acrylic acid units.
Zn^{2+}	zinc salts of above copolymers.

5.4 *THERMAL VOLATILISATION ANALYSIS*

In TVA powdered copolymer samples, of approximately 60 mg, were heated to 500°C, at 10°C/min, under vacuum. The vacuum line, illustrated in **Fig. 2.3**, contained five Pirani gauges situated after traps cooled to 0°C, -45°C, -75°C, -100°C and -196°C respectively.

The results obtained, together with the amounts of cold ring and liquid fractions collected, are given in **Figs. 5.7** to **5.9** and **Table 5.2**.

The TVA curves consist of a single peak due to the main decomposition step in the copolymers. The very small Pirani gauge response between 80°C and 150°C, in the copolymers containing 11.8% acrylic acid units, is due to the release of either solvent or moisture trapped in these samples.

The Pirani gauges after the 0°C and -45°C traps show larger pressure readings than those after the other traps due to the condensation of styrene, the major volatile degradation product, in the colder traps. The Pirani gauge response after the -45°C trap is sensitive to any changes in the temperature of this trap. The amount of styrene condensed in it varied with any small variation in temperature.

From previous work on the degradation of polystyrene it is believed that all the products resulting from the degradation of the styrene parts of the copolymer are condensed by the traps cooled to -75°C, -100°C and -196°C. The pressure readings obtained on the Pirani gauges after the -75°C, -100°C and -196°C traps are only due to the products resulting from the degradation of the acrylic acid or zinc acrylate units within the copolymer, while the gauges after the 0°C and -45°C traps register pressures due to the degradation products of both types of monomer unit in the copolymer.

The first peak for the gauges after the -45°C, -75°C and -100°C traps is concurrent with the maximum pressure reading for the gauge after the 0°C trap and is due to the formation of volatiles from copolymer decomposition. The shoulder only found in the zinc salt copolymers, at a temperature approximately 25°C higher than the main peak is due to the decomposition of zinc oxide formed during the copolymer degradation. In the presence of carbon, zinc oxide will be reduced to zinc with the formation of carbon monoxide or carbon dioxide. At this temperature most of the polymer sample will have degraded which may mean that zinc oxide is in excess compared to any carbonaceous material in the degradation tube resulting in the formation of a mixture of carbon monoxide and carbon dioxide. The separation of the pressure readings after the -196°C and -100°C traps suggests both carbon monoxide and carbon dioxide are being formed at this stage. The size of this shoulder is dependent on the metal content of the copolymers. It is largest for the copolymer containing 11.8% acrylic acid units but is barely discernible for the copolymer with 1.7% acrylic acid units. The only non-condensable gas identified was carbon monoxide.

The residue of after heating to 500°C was in all cases found to be very small. Zinc metal formed as degradation products was volatile under vacuum at the elevated oven temperature and was condensed by the cold ring. In the results table the weight of cold ring fraction obtained for the zinc salt copolymers does not contain the amount of zinc.

It is difficult to make comment on the change in stability of the copolymers with variation in acrylic acid and zinc content from the results obtained. Between 30% and 40% of the weight of volatile products are condensed by the cold ring and do not register on the Pirani gauges.

Changing the amount of acrylic acid units in the copolymers appears to have little effect on the onset temperature for volatile evolution or the temperature of maximum rate of evolution of volatile degradation products. The onset temperature for volatile evolution occurred at 325°C for all the copolymers. The results obtained for the maxima for the three copolymers all fell within a range of 3°C. These were 419°C for the copolymer with 1.7% acrylic acid units, 422°C for the copolymer with 5.8% acrylic acid units and 420° for the copolymer containing 11.8% acrylic acid units.

The results agree with the thermogravimetric analysis in that the zinc salts of the copolymers have both a higher onset temperature for volatile evolution and a higher temperature of maximum evolution of volatiles, compared with the corresponding acid copolymer.

The onset temperatures were approximately 340°C for the copolymer with 1.7% acrylic acid units, 335°C for the copolymer with 5.8% acrylic acid units and 350°C for the copolymer with 11.8% acrylic acid units. These results are about 10°C to 15°C higher than for the unneutralised copolymers, with the greatest difference (15°C), seen for the copolymers containing 1.7 and 11.8% acrylic acid units.

In degradation under TVA conditions no trend in the change in thermal stability with increasing metal content was seen in the zinc salts of the copolymers. The zinc salt of the copolymer with 1.7% acrylic acid units had its maximum at 428°C, while the 5.8% acrylic acid unit and 11.8% acrylic acid unit zinc salt copolymers both had their maxima at 433°C. These maxima temperatures are greater than those for the corresponding acid copolymers by 9, 12 and 11°C respectively.

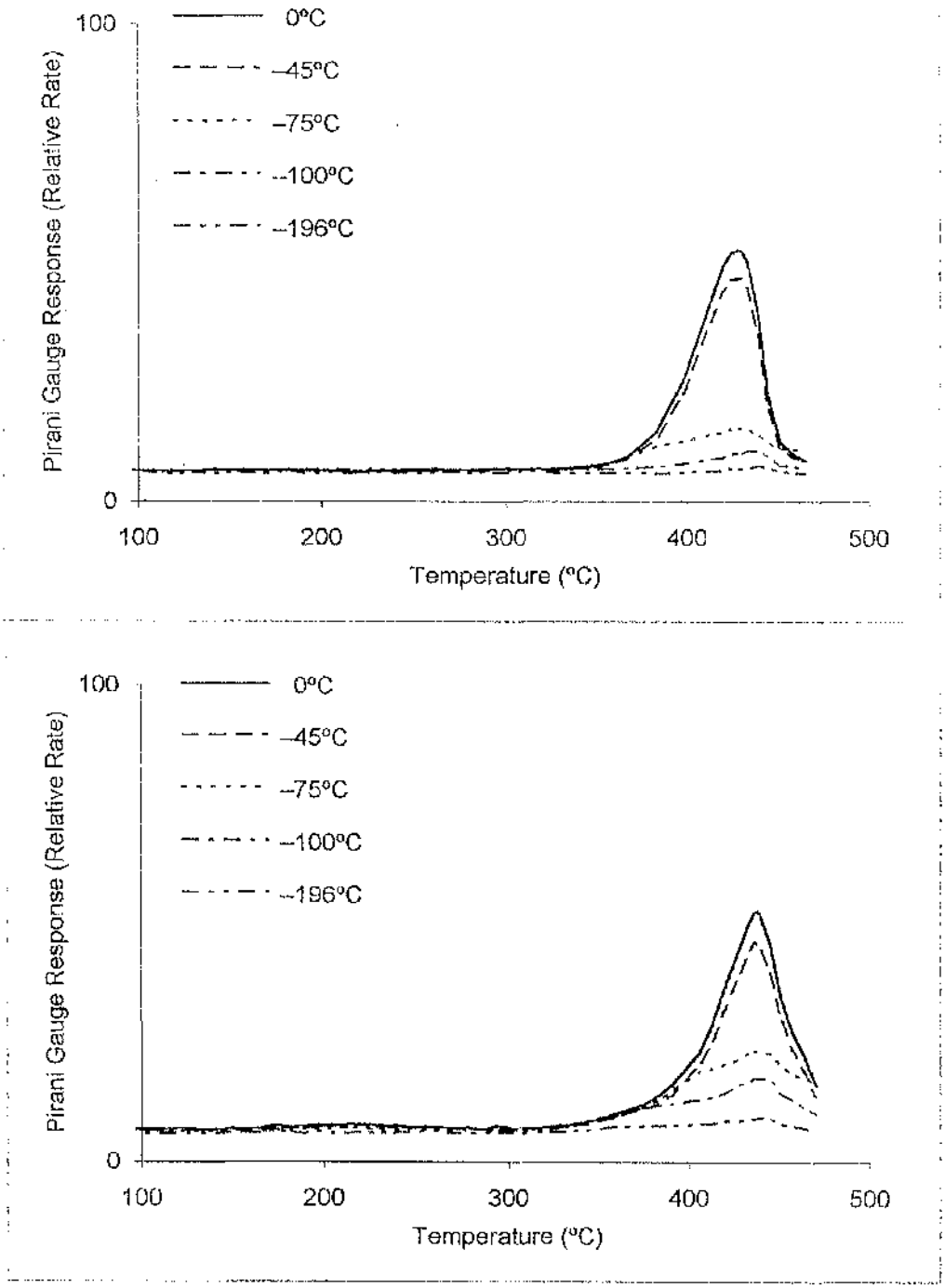


Fig. 5.7 TVA curves (heating rate 10°C/min to 500°C) obtained for the styrene/acrylic acid copolymer containing 1.7% acrylic acid units (top) and its zinc salt (bottom).

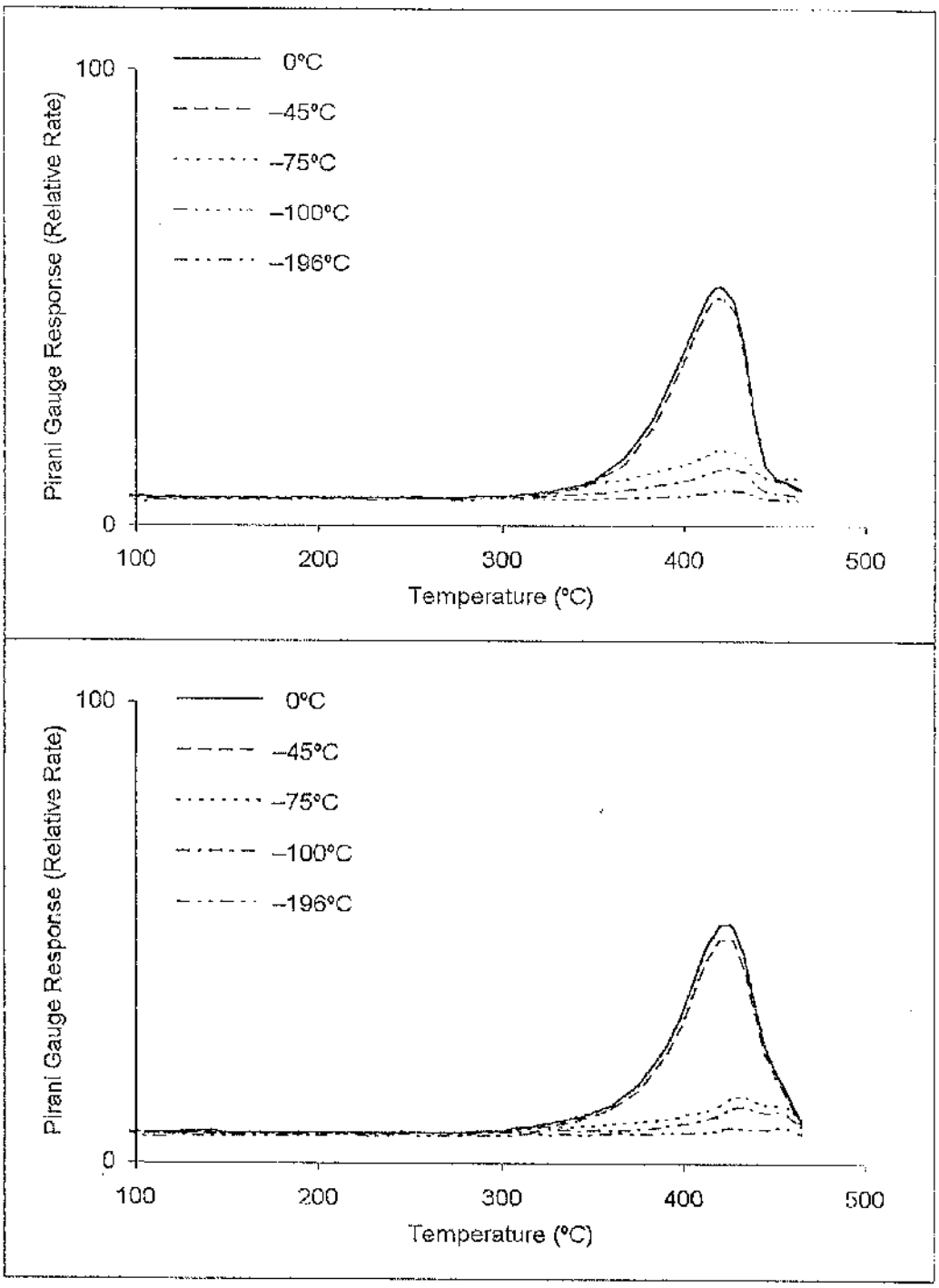


Fig. 5.8 TVA curves (heating rate 10°C/min to 500°C) obtained for the styrene/acrylic acid copolymer containing 5.8% acrylic acid units (top) and its zinc salt (bottom).

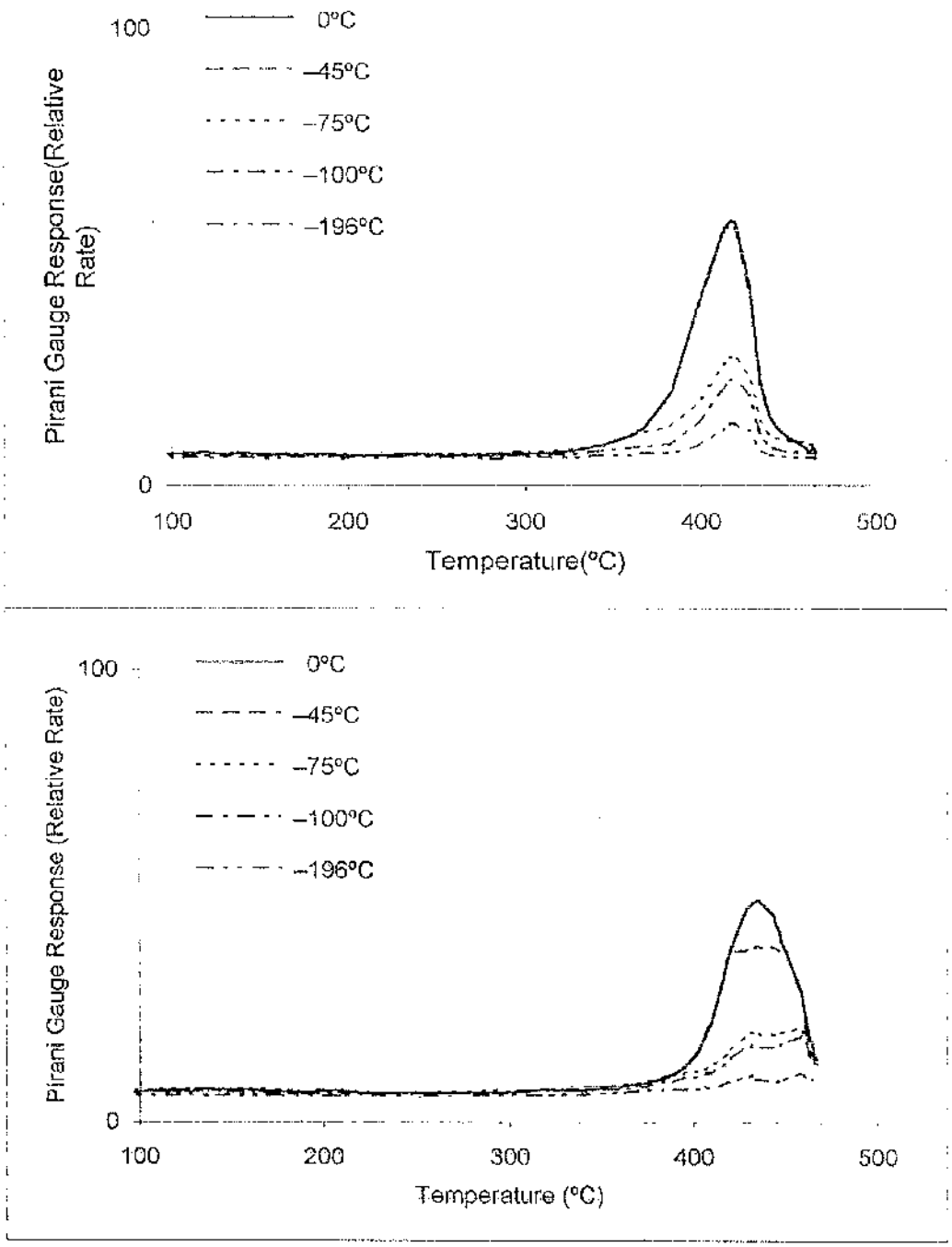


Fig 5.9 TVA curves (heating rate 10°C/min to 500°C) obtained for the styrene/acrylic acid copolymer containing 11.8% acrylic acid units (top) and its zinc salt (bottom).

copolymer	T_{onset} (°C)	T_{max} (°C)	% cold ring fraction	% liquid finger
1.7% AA/ St	325	419	39.3	56.2
1.7% AA/ St+Zn^{2+}	340	428	31.1	59.0
5.8% AA/ St	325	421	40.0	49.2
5.8% AA/ St+Zn^{2+}	335	433	35.1	56.4
11.8% AA/ St	335	422	41.4	47.9
11.8% AA/ St +Zn^{2+}	350	433	33.9	51.9

Table 5.2 TVA data for styrene / acrylic acid copolymers and their zinc salts.

1.7% AA/ St	acrylic acid/styrene copolymer containing 1.7% acrylic acid units.
5.8% AA/ St	acrylic acid/styrene copolymer containing 5.8% acrylic acid units.
11.8% AA/St	acrylic acid/styrene copolymer containing 11.8% acrylic acid units.
Zn^{2+}	zinc salts of above copolymers.
%	mole % acrylic acid units in copolymer

5.5 IDENTIFICATION OF DEGRADATION PRODUCTS

5.5.1 Sub-ambient Thermal Volatilisation Analysis

The technique of sub-ambient TVA (SATVA) described in chapter two was used for partial separation and collection of the degradation products from the TVA experiments. The SATVA traces obtained for the copolymers are given in **Figs. 5.10** to **5.12** with the identified degradation products listed in **Tables 5.4** to **5.9**.

The early products evolved were gaseous products resulting from the decomposition of the acrylic acid or zinc acrylate units in the copolymer. The peak between 11-14 minutes consisted of carbon dioxide and ketene while the second smaller peak after this was due to formaldehyde or acetaldehyde. As would be expected, if the substances were derived from the decomposition of the acrylic groups, these peaks tended to be larger for the copolymers containing 5.8% and 11.8% acrylic acid.

The larger main peak was collected as a liquid fraction for GC-MS analysis. The gas chromatograms obtained are given in **Figs. 5.13** to **5.15**. The major component in the liquid fraction was styrene with toluene and α-methylstyrene as the other significant products. Quantitative analysis showed the styrene content to be between 95% and 98% of the total amount of products in the liquid fraction. The relative amounts of the three main products in the liquid fraction are given in **Table 5.3**.

The only liquid fraction product found by GC-MS that could be related to the decomposition of the acrylic acid groups was benzaldehyde.

The other liquid products found by GC-MS analysis in very small amounts totalling less than 1% of the liquid fraction, consisted of a range of 3 and 4

carbon atom alkenyl-substituted benzenes resulting from the degradation of the styrene portions of the copolymer. The type of structures identified are illustrated in **Fig. 5.16**. Due to the small amount of material and the similarity of their mass spectra, many of the compounds detected in gas chromatography could not be identified or the isomers differentiated. The total amounts of this type of product were found to be less than 0.5% of the liquid fraction.

copolymer	toluene	styrene	α-methylstyrene
1.7% AA/St	1.36%	98.12%	0.30%
1.7% AA/St + Zn^{2+}	2.93%	95.71%	0.80%
5.8% AA/St	1.58%	97.62%	0.32%
5% AA/St + Zn^{2+}	1.67%	96.86%	0.76%
11.8% AA/St	2.14%	96.14%	0.50%
11.8% AA/St + Zn^{2+}	2.43%	95.92%	1.00%

Table 5.3 Major products found in the liquid fraction in the SATVA separation of products from degradation to 500°C under TVA conditions.

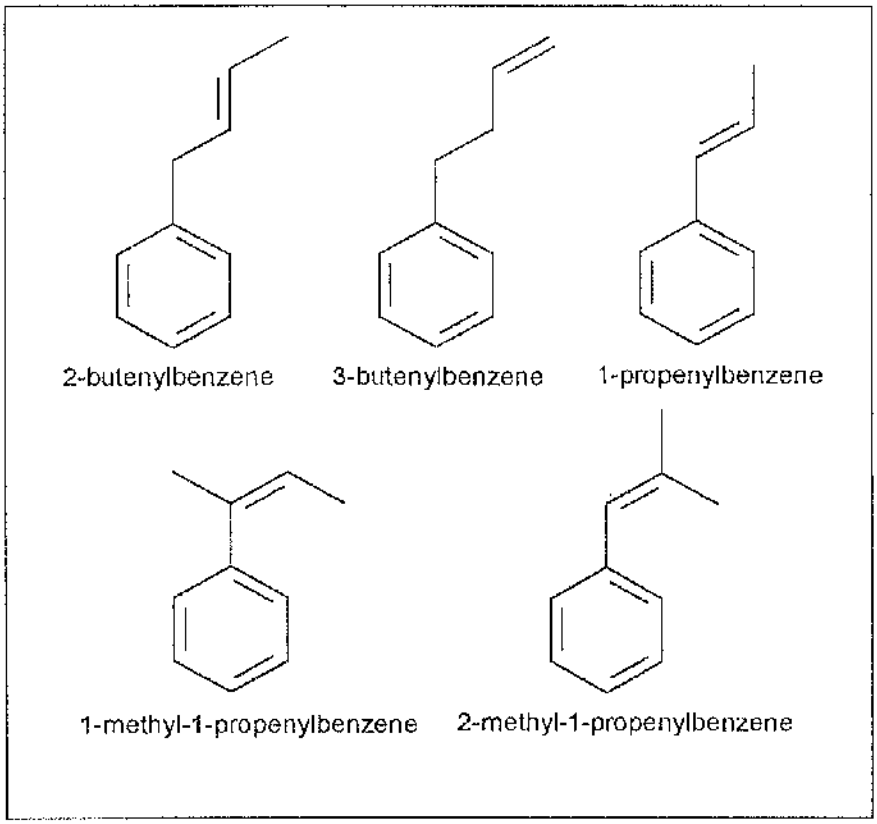


Fig. 5.16 Minor products found in the liquid fraction.

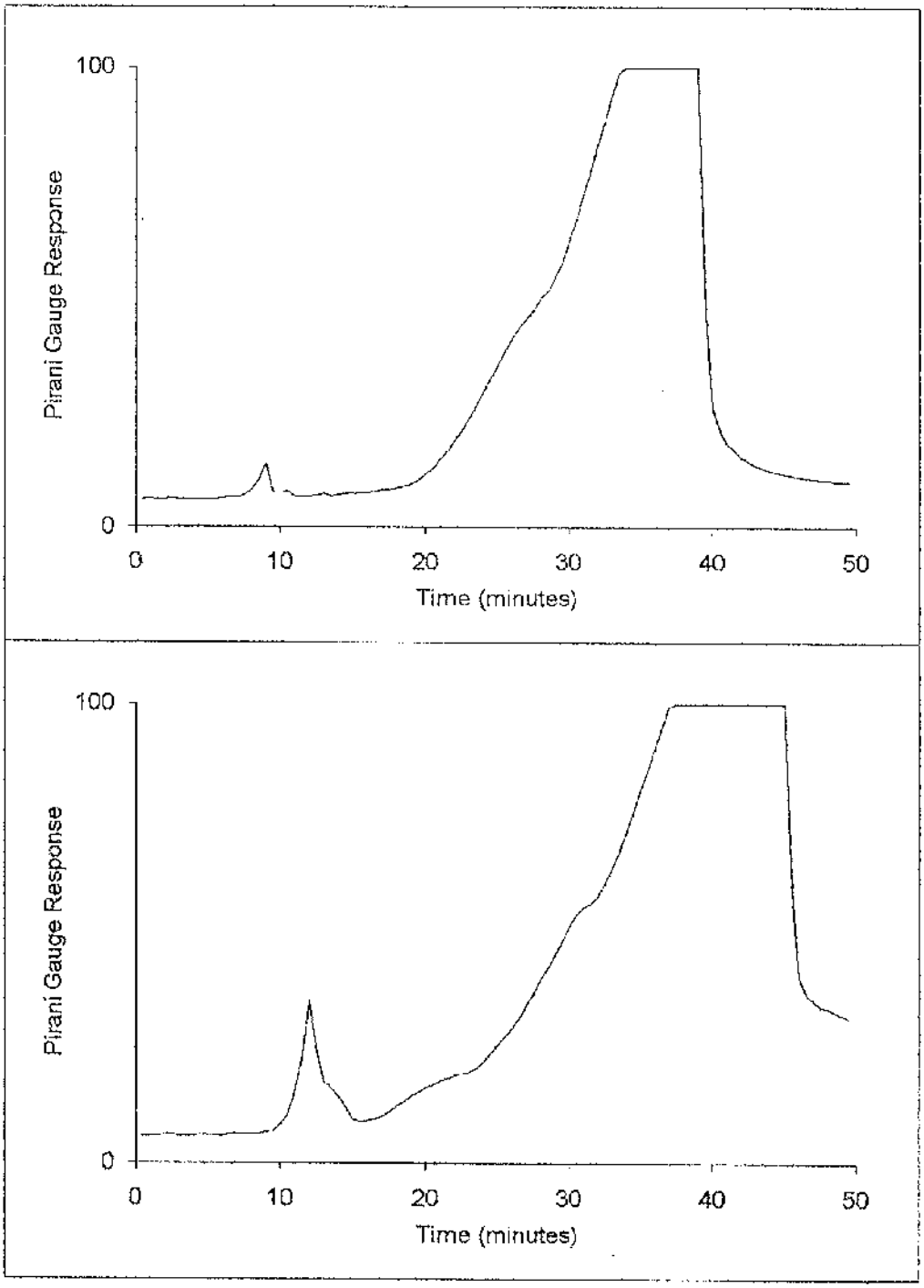


Fig. 5.10 SATVA curves of the products of degradation, obtained under TVA conditions, of the styrene/acrylic acid copolymer containing 1.7% acrylic acid units (top) and its zinc salt (bottom).

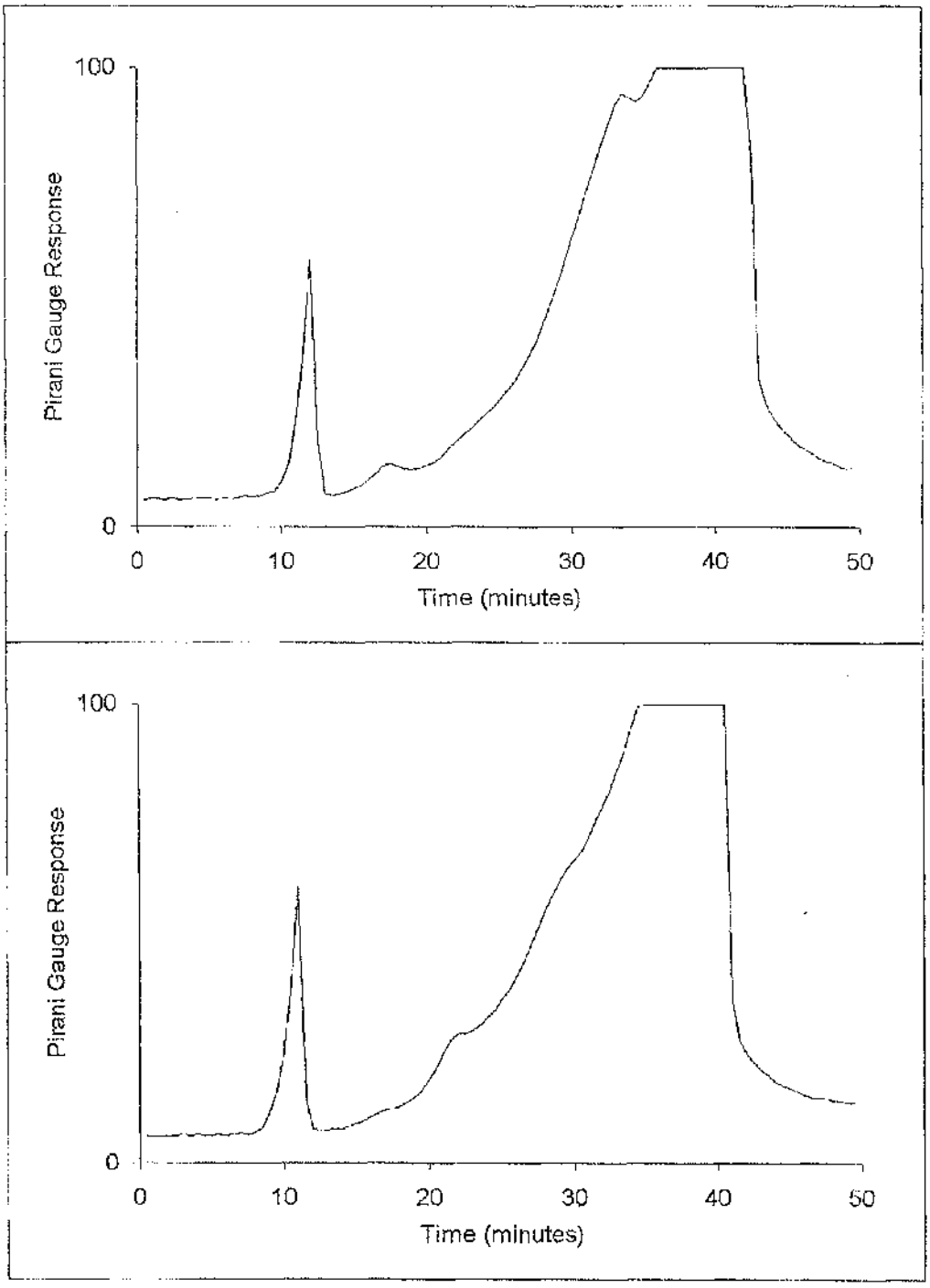


Fig. 5.11 SATVA curves of the products of degradation, obtained under TVA conditions, of the styrene/acrylic acid copolymer containing 5.8% acrylic acid units (top) and its zinc salt (bottom).

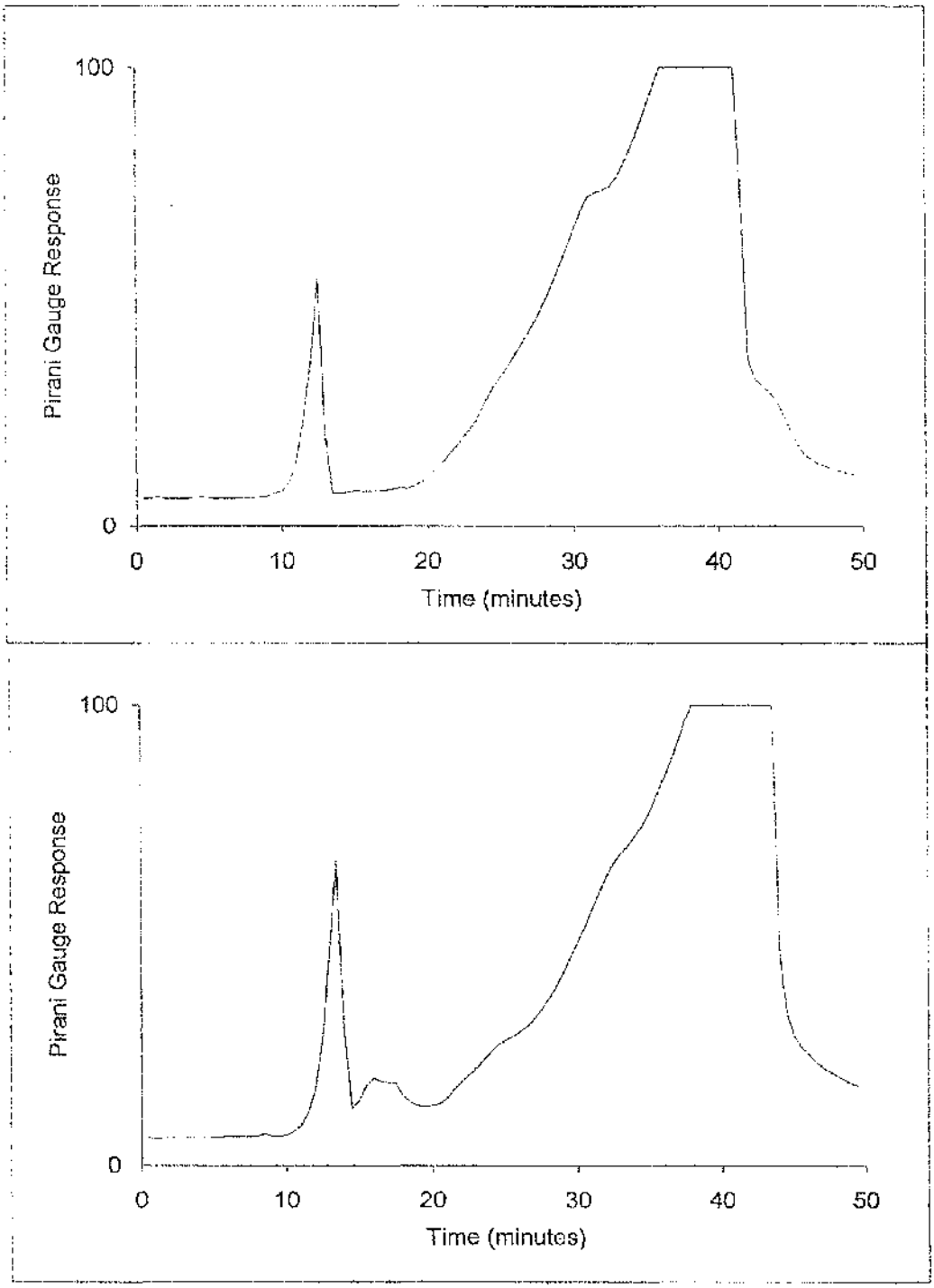


Fig. 5.12 SATVA curves of the products of degradation, obtained under TVA conditions, of the styrene/acrylic acid copolymer containing 11.8% acrylic acid units (top) and its zinc salt (bottom).

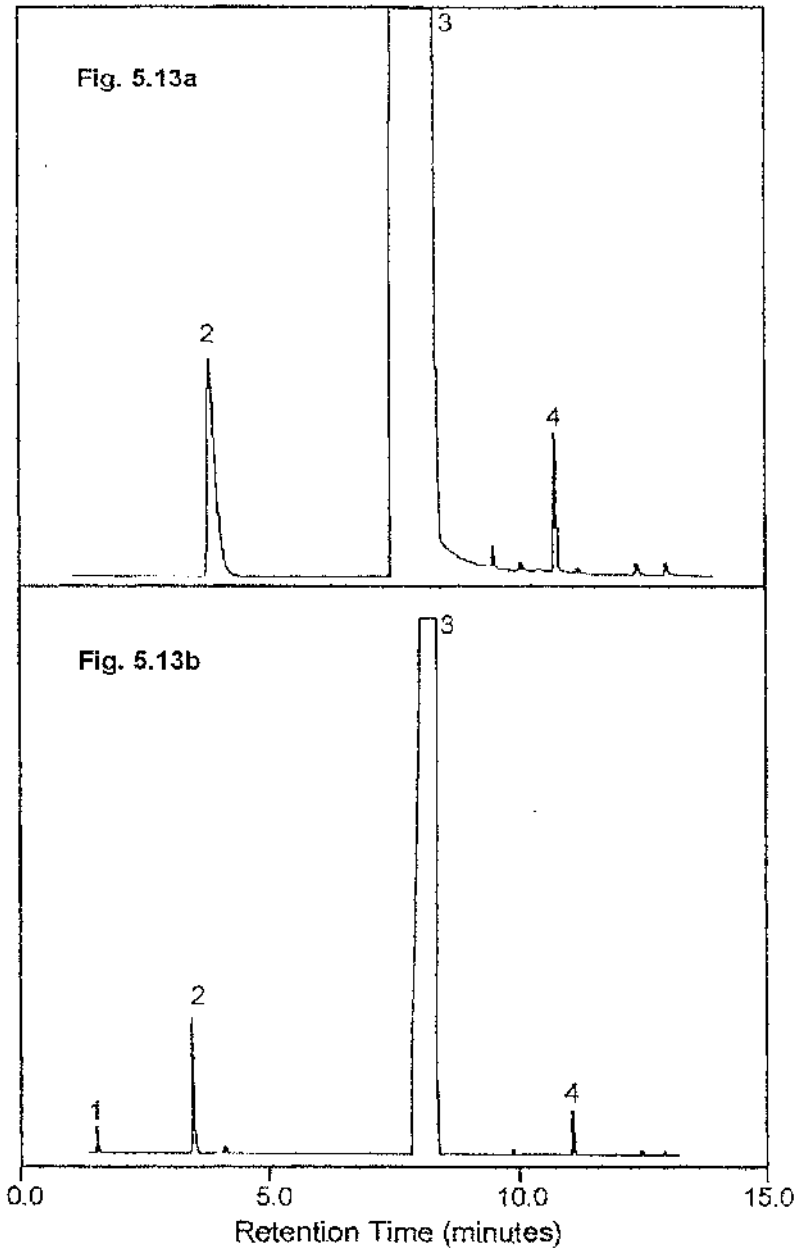


Fig 5.13 Gas chromatograms of the liquid fractions obtained from the SATVA separations of products of degradation under TVA conditions of the acrylic acid/styrene copolymer containing 1.7% acrylic acid units (**Fig. 5.13a**) and its zinc salt (**Fig. 5.13b**).

Peak Assignments

1 benzene, **2** toluene, **3** styrene, **4** α-methylstyrene.

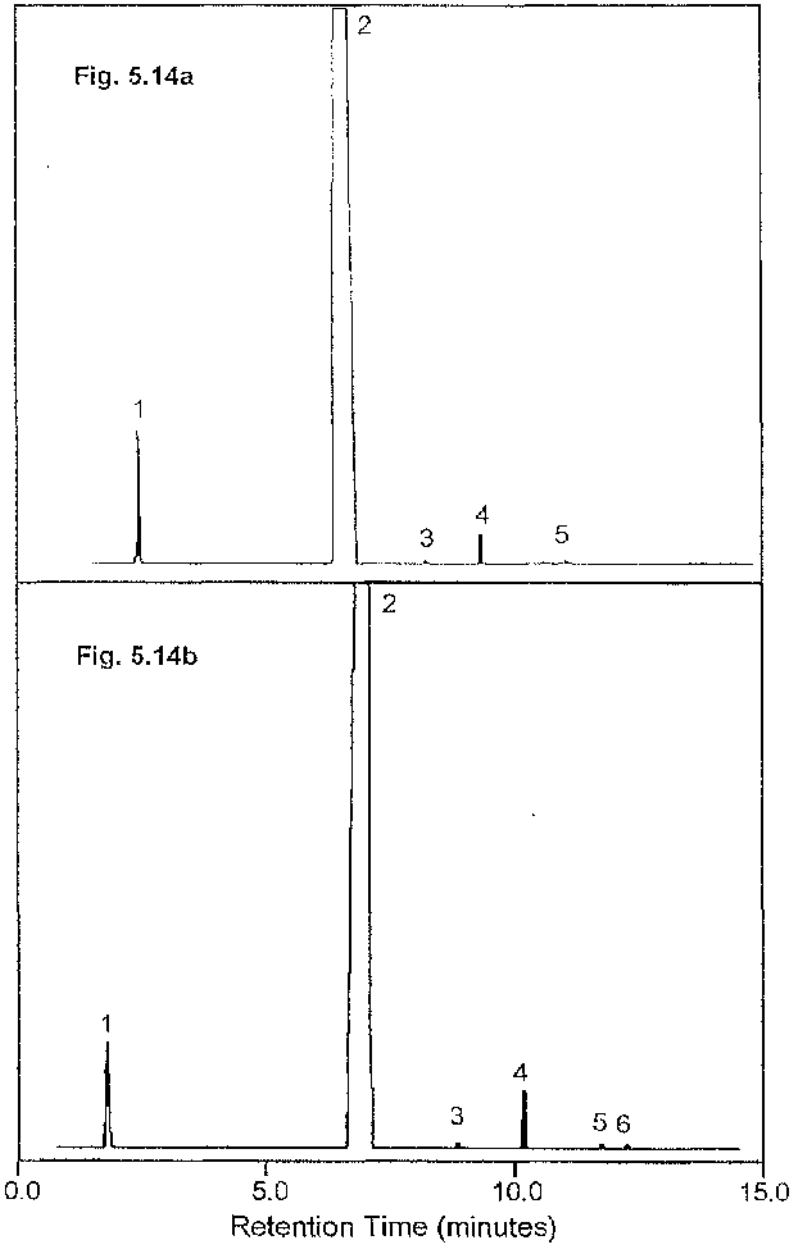


Fig 5.14 Gas chromatograms of the liquid fractions obtained from the SATVA separations of products of degradation under TVA conditions of the acrylic acid/styrene copolymer containing 5.8% acrylic acid units (**Fig. 5.14a**) and its zinc salt (**Fig. 5.14b**).

Peak Assignments

1 toluene, **2** styrene, **3** benzaldehyde, **4** α-methylstyrene, **5** 1-propenylbenzene, **6** 3-butenylbenzene.

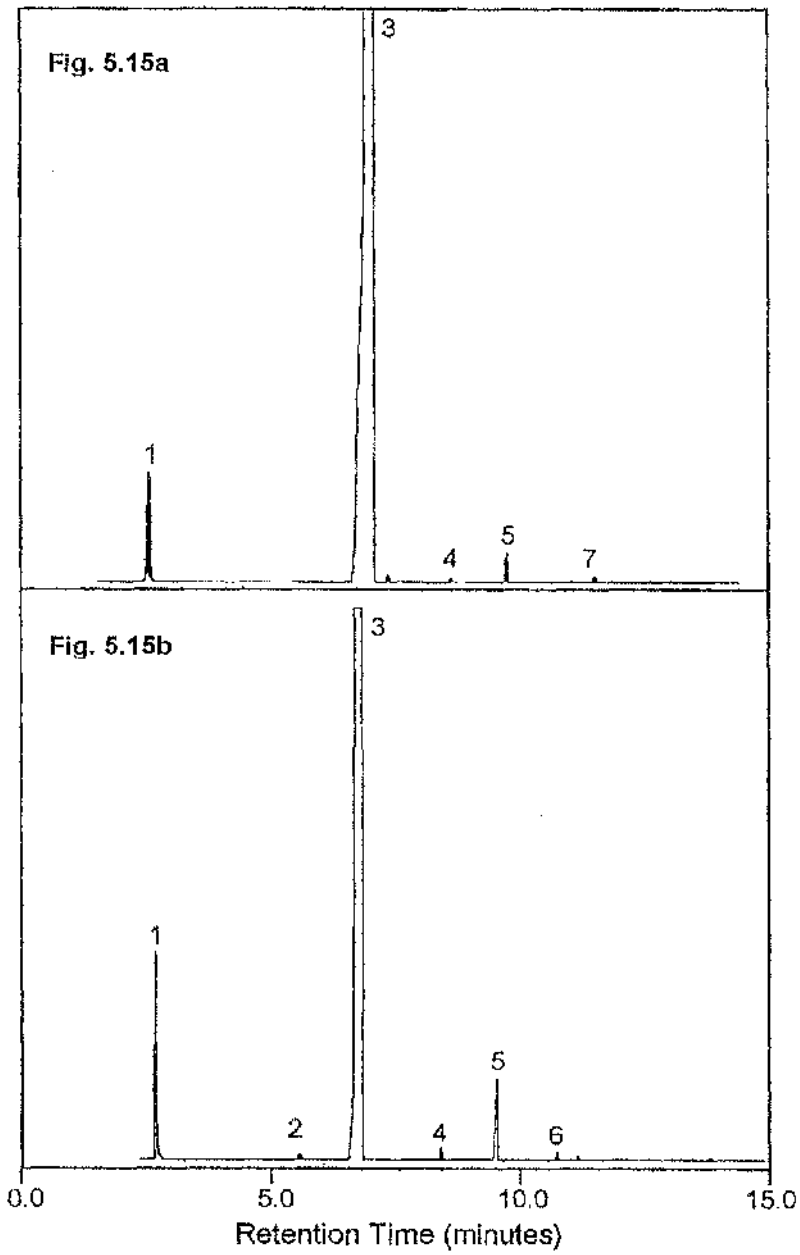


Fig 5.15 Gas chromatograms of the liquid fractions obtained from the SATVA separations of products of degradation under TVA conditions of the acrylic acid/styrene copolymer containing 11.8% acrylic acid units (**Fig.5.15a**) and its zinc salt (**Fig. 5.15b**).

Peak Assignments

1 toluene, **2** ethylbenzene, **3** styrene, **4** benzaldehyde , **5** α-methyl-styrene, **6** 1-propenylbenzene, **7** 3-butenylbenzene.

5.5.2 COLD RING FRACTIONS

The cold ring fractions obtained by the degradation of the copolymers under TVA conditions were studied by examining their infra-red and mass spectra. The mass spectra obtained are given in **Figs. 5.17** to **5.19** and the infra-red spectra in **Figs. 5.20** and **5.21**.

5.5.2a Mass Spectra

The results obtained from mass spectroscopy are consistent with the presence of styrene oligomers. Peaks in the spectra at m/z = 208, 312, 416 and 520 are due to oligomers containing from 2 to 5 styrene monomer units. The decrease in intensity of the peaks of the molecular ions indicates the abundance of each type of oligomer decreased as the number of monomer units increased, with the dimer and trimer the most abundant types of oligomer while tetramer and pentamer are minor products. The styrene pentamer was only observed in the cold ring fraction of the copolymer. This is because of the mechanism by which these oligomers are formed.

In Fig. **5.30** the macroradical (D) formed by main chain scission undergoes further decomposition by intramolecular hydrogen transfer. This type of reaction is most favoured with the closest tertiary hydrogen atom. As the size of the chain increases and the distance between radical and hydrogen atom increases the hydrogen atom abstraction reaction becomes less sterically favourable and as a result oligomers containing four and five styrene units become less abundant.

No other types of compound were identified from the mass spectra of the cold ring fractions.

5.5.2b Infra-red Spectra

The cold ring fractions were prepared for infra-red analysis by first dissolving them in dichloromethane. The resulting solutions were added drop wise to a sodium chloride plate. Evaporation of the solvent resulted in a thin layer of the cold ring fraction being left on the salt plate. The infra-red spectra of the cold ring fractions are given in **Figs. 5.20 and 5.21**

The infra-red spectra have all the absorptions consistent with the presence of styrene oligomers as found in mass spectral analysis. These include the aromatic C-H stretching bands above 3000 cm^{-1}, the saturated C-H stretching bands below 3000 cm^{-1} three aromatic ring bands at 1608 cm^{-1} 1580 cm^{-1} and 1497 cm^{-1} and C-H out of plane vibrations at 763 cm^{-1} and 701 cm^{-1}

One of the main differences between the cold ring fractions and the starting copolymers are the absence of the absorption bands due to the carboxylic acid or zinc carboxylate groups. These were the carboxylic acid carbonyl absorption at 1710 cm^{-1} and the broad carboxylate symmetrical and anti-symmetrical stretching bands at 1560 cm^{-1} and 1440 cm^{-1} These were not found in the cold ring fractions of any of the polymers. They were replaced by two bands at 1685 cm^{-1} and 1724 cm^{-1} except in the acid copolymer containing 11.8% acrylic acid units, where a broad absorption with a maximum at 1697 cm^{-1} was present. These bands therefore indicate the presence of α-β-unsaturated carboxylic acid groups in the oligomers **Fig. 5.22.**

No evidence for the existence of carboxylic acid groups was found in mass spectral analysis but these would not give a strong molecular ion peak such as is found in the aromatic compounds.

The other difference in the spectra of cold ring and starting copolymers was the absorption at 1630 cm^{-1} due to the carbon-carbon double bond, conjugated with the aromatic ring, in the styrene oligomers.

Analysis of the relative amounts of cold ring fraction and cold finger obtained show an increase in the amount of cold ring obtained as the number of acrylic acid units is increased. The presence of acrylic acid units will act as a block to the unzipping process occurring in the formation of monomer, the major product collected in the cold finger. The larger the number of acid groups present, the more likely it is that any unzipping reaction will be stopped.

The amount of cold ring obtained for the zinc salt is less than that obtained for the corresponding copolymer. The crosslinking zinc ions will result in a more rigid structure with reduced chain flexibility, which will inhibit the intramolecular transfer reactions that result in the formation of oligomers.

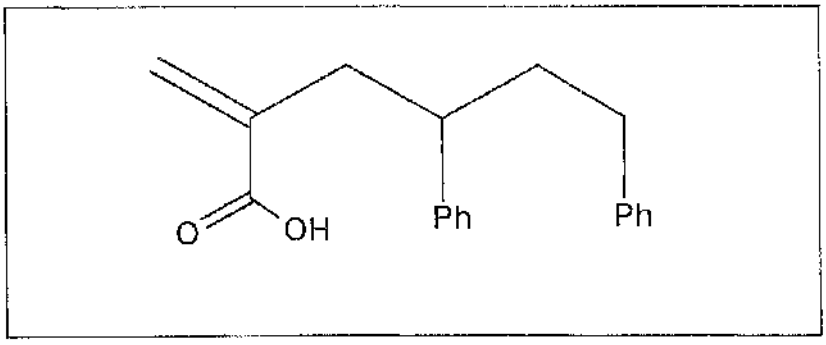


Fig. 5.22 Possible structure of unsaturated carboxylic acid group containing oligomers.

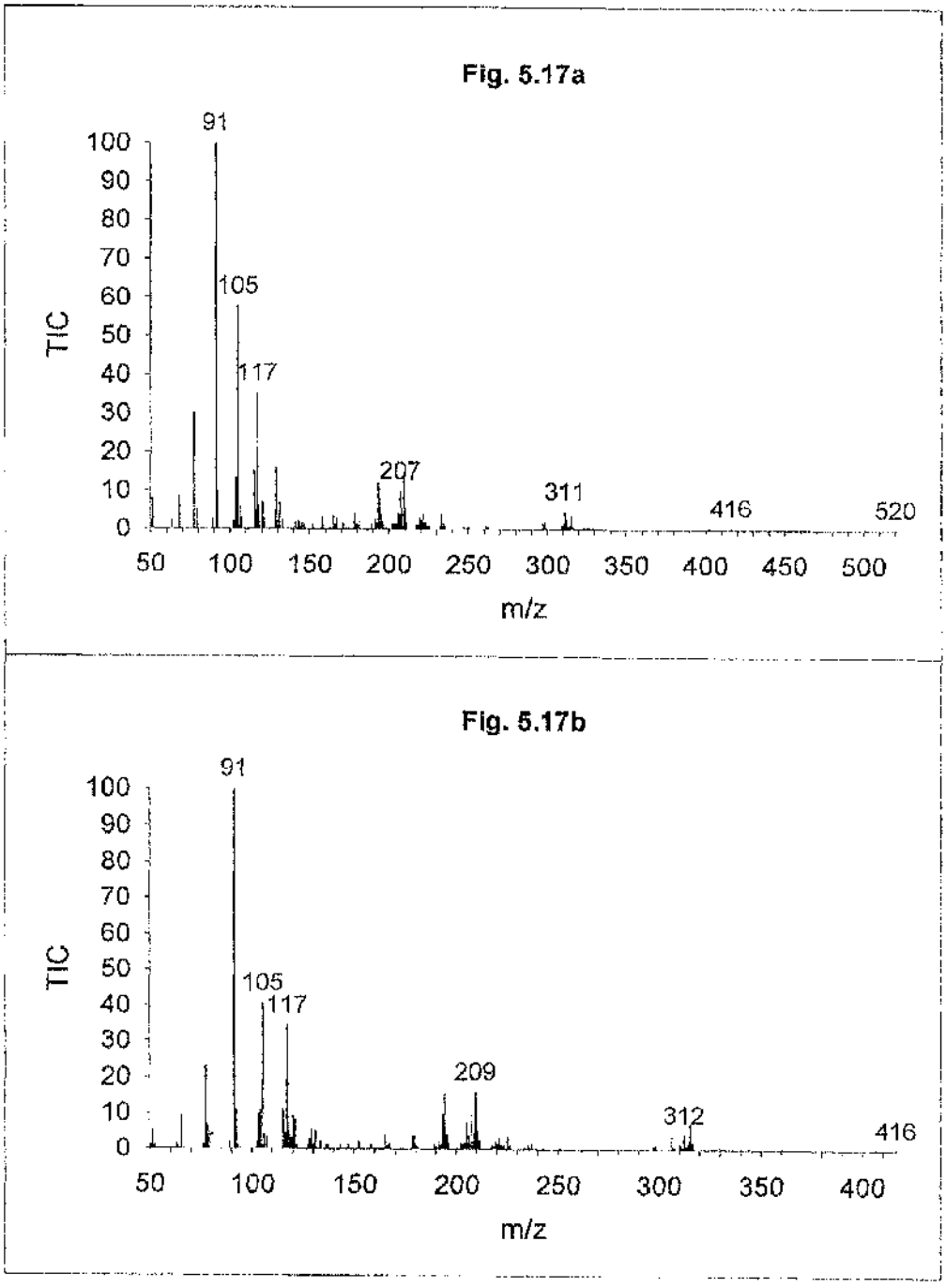


Fig. 5.17a&b Mass spectra of cold ring fraction products of degradation, obtained by heating to 500°C under TVA conditions, of the styrene/acrylic acid copolymer, containing 1.7% acrylic acid units (Fig 5.17a) and its zinc salt (5.17b).

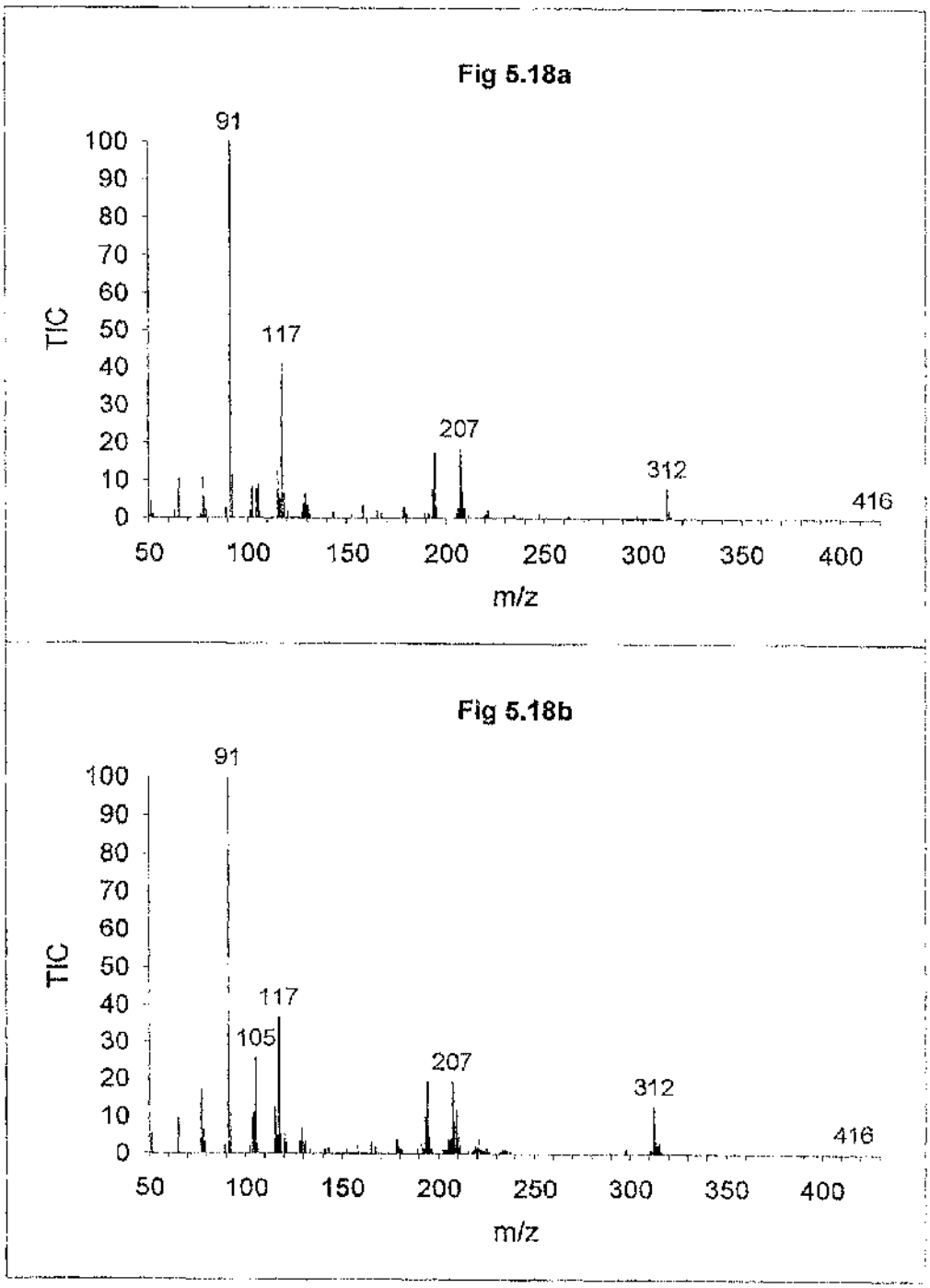


Fig 5.18a&b Mass spectra of cold ring fraction products of degradation, obtained by heating to 500°C under TVA conditions, of the styrene/acrylic acid copolymer, containing 5.8% acrylic acid units (Fig 5.18a) and its zinc salt (5.18b).

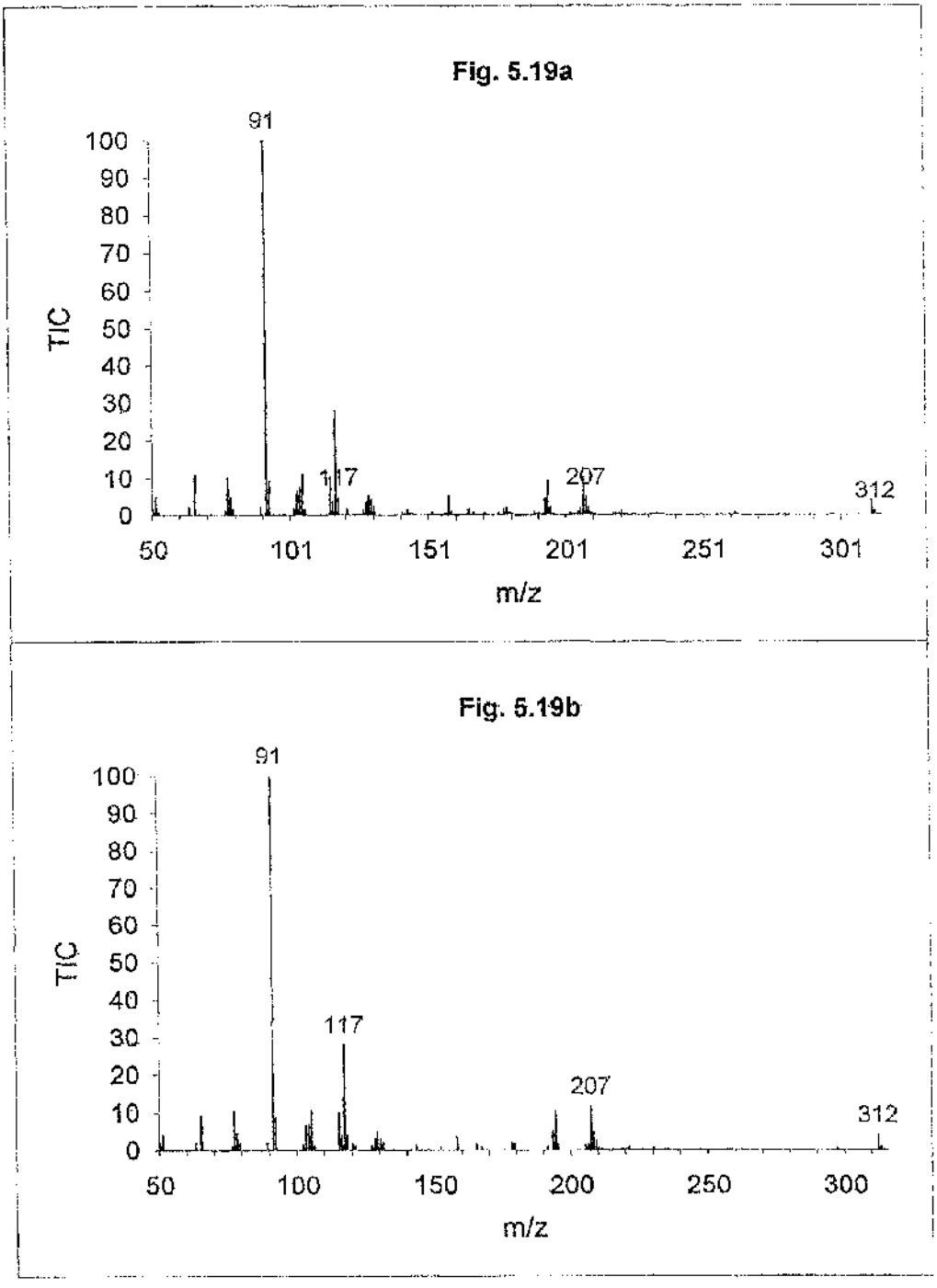


Fig. 5.19a&b Mass spectra of cold ring fraction products of degradation, obtained by heating to 500°C under TVA conditions, of the styrene/acrylic acid copolymer, containing 11.8% acrylic acid units (Fig 5.19a) and its zinc salt (5.19b).

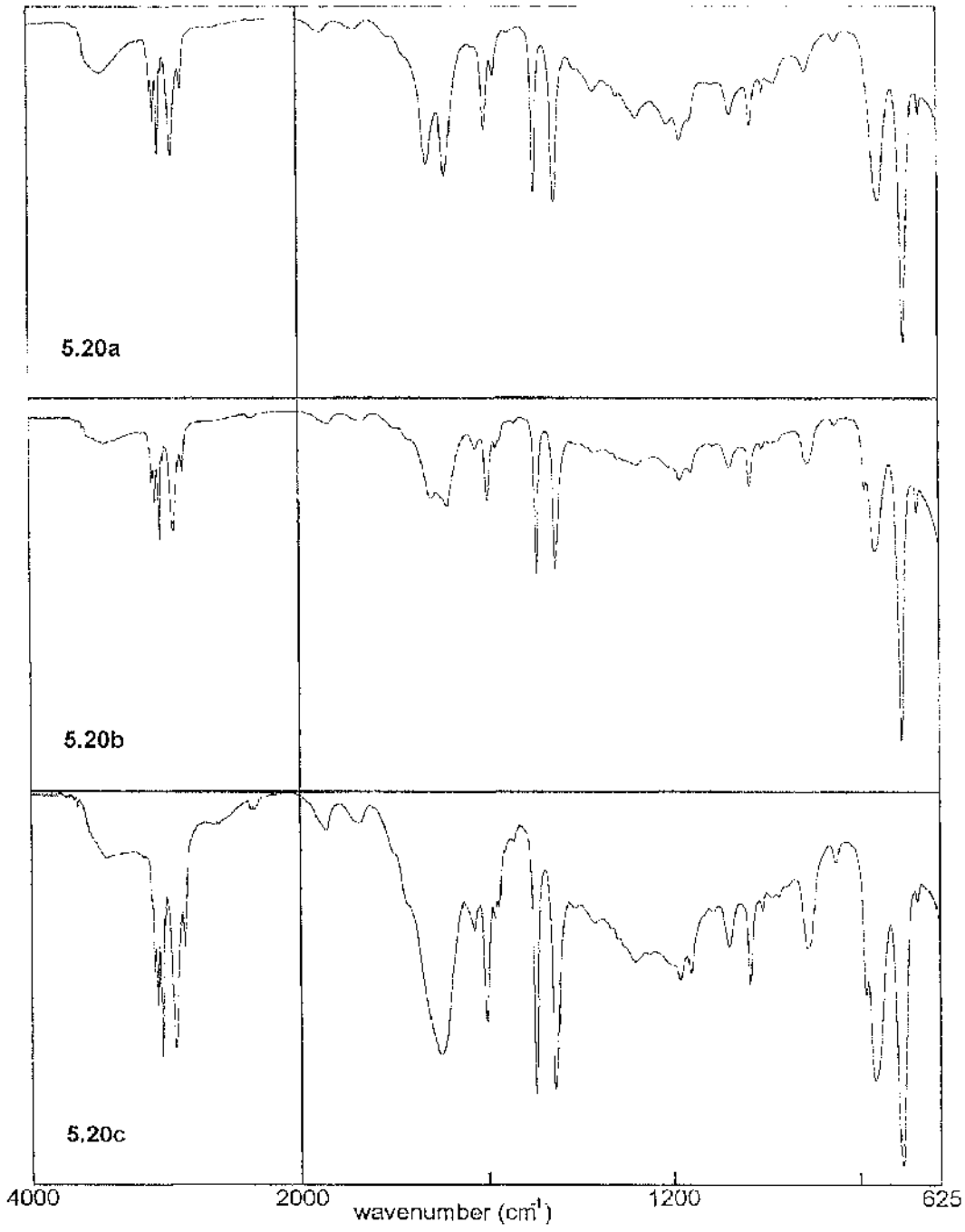


Fig. 5.20a Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the acrylic acid/styrene copolymer containing 1.7% acrylic acid units.

Fig. 5.20b Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the acrylic acid/styrene copolymer containing 5.8% acrylic acid units.

Fig. 5.20c Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the acrylic acid/styrene copolymer containing 11.8% acrylic acid units.

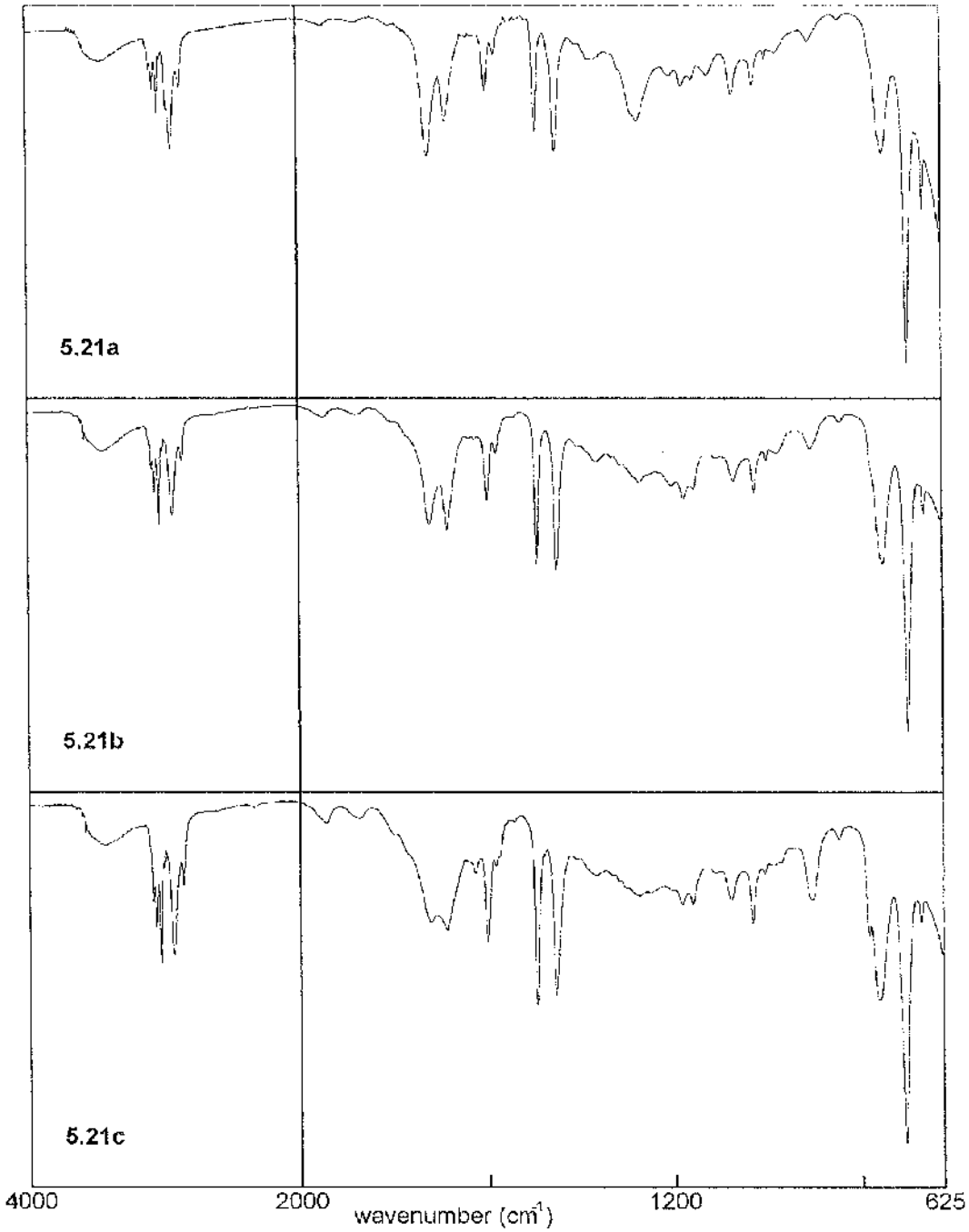


Fig. 5.21a Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the zinc salt of the acrylic acid/styrene copolymer containing 1.7% acrylic acid units.

Fig. 5.21b Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the zinc salt of the acrylic acid/styrene copolymer containing 5.8% acrylic acid units.

Fig. 5.21c Infra-red spectrum of cold ring fraction from the degradation, under TVA conditions, of the zinc salt of the acrylic acid/styrene copolymer containing 11.8% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide carbon dioxide ketene formaldehyde	toluene styrene α-methylstyrene	styrene oligomers

Table 5.4 Products of degradation to 500°C of styrene/acrylic acid copolymer containing 1.7% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide carbon dioxide acetaldehyde	benzene toluene styrene α-methylstyrene	styrene oligomers

Table 5.5 Products of degradation to 500°C of the zinc salt of the styrene/acrylic acid copolymer containing 1.7% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide	toluene	styrene oligomers
carbon dioxide	styrene	
ketene	benzaldehyde	
formaldehyde	α-methylstyrene	
acetaldehyde	1-propenylbenzene	

Table 5.6 Products of degradation to 500°C of styrene/acrylic acid copolymer containing 5.8% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide	toluene	styrene oligomers
carbon dioxide	ethylbenzene	
ketene	styrene	
acetaldehyde	benzaldehyde	
benzene	α-methylstyrene	
	1-propenylbenzene	
	3-butenylbenzene	

Table 5.7 Products of degradation to 500°C of the zinc salt of the styrene/acrylic acid copolymer containing 5.8% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide carbon dioxide ketene formaldehyde benzene	toluene styrene benzaldehyde α-methylstyrene 3-butenylbenzene	styrene oligomers

Table 5.8 Products of degradation to 500°C of styrene/acrylic acid copolymer containing 11.8% acrylic acid units.

Gaseous Products identified by IR./MS	Liquid Products identified by GC-MS	Cold Ring Fraction identified by IR./MS
carbon monoxide carbon dioxide ketene formaldehyde	toluene ethylbenzene styrene benzaldehyde α-methylstyrene 2-propenylbenzene	styrene oligomers

Table 5.9 Products of degradation to 500°C of the zinc salt of the styrene/acrylic acid copolymer containing 11.8% acrylic acid units.

5.5 *ISOTHERMAL HEATING EXPERIMENTS*

It was observed from thermogravimetry that the initial rate of weight loss appeared to be greater and occur at lower temperatures for the acid copolymers than for their corresponding zinc salt. To investigate this further copolymer samples were heated isothermally, under vacuum, for varying lengths of time with the weight of the polymer recorded before and after heating.

The temperature chosen for the isothermal heating experiments was 350°C as this was close to the observed onset temperature of degradation of all the polymers, found in the programmed heating TVA experiments. Polymer samples of approximately 50 mg were heated under vacuum for between 30 minutes and 2 hours with the weight of sample recorded before and after the experiment.

.A comparison of the results obtained for the acid copolymers (**Fig. 5.23**) suggests that if allowances are made for experimental error in weighing of the samples there is little change in the rate of degradation at 350°C as the number of acrylic acid units in the copolymers is increased.

A difference in the rate of weight loss was seen for the copolymers with different numbers of zinc acrylate groups. The rate of weight loss at 350°C decreased with increasing numbers of zinc acrylate groups (**Fig. 5.24**).

A significant decrease in the rate of degradation is seen when comparing the copolymers containing 5.8% and 11.8% acrylic acid units with their zinc salts (**Figs. 5.26&27**). The results obtained show that at 350°C, the rate of degradation of the copolymers is approximately twice that of their zinc salts. The copolymer containing 1.7% acrylic acid units (**Fig. 5.25**) shows no change in the rate of degradation by changing it to its zinc salt.

The infra-red spectra of the acid copolymer containing 5.8% acrylic acid units after heating for 0.5, 1.0, 1.5 and 2.0 hours at 350°C are given in **Fig. 5.28**. The spectra were recorded after the samples had cooled to room temperature.

The most interesting change occurring in the acid copolymer sample as it is heated is the greater decrease in the intensity of the bands at 1742 cm^{-1} and 1704 $cm,^{-1}$ due to the carbonyl groups of the carboxylic acids, compared to the absorption bands 1600 $cm,^{-1}$ 1580 cm^{-1} and 1490 cm^{-1} due to aromatic ring of the styrene portion of the copolymer. These results were also found for the acid copolymers containing 1.7% and 11.8% acrylic acid units.

The relative intensity of the two carbonyl absorption bands has also changed. The non hydrogen bonded carboxylic acid carbonyl absorption at 1742 cm^{-1} (described in section 3.9.3) has increased in intensity relative to the hydrogen bonded carbonyl absorption at 1704 $cm.^{-1}$ This would be expected because the decomposition of carboxylic acid groups reduce their total number and the probability of a hydrogen bonded dimer being formed decreases. Nyquist[27] found that on heating a styrene/acrylic acid copolymer the number of hydrogen bonded dimers decreased but on cooling the number of hydrogen bonded dimers returned to its original level, so this should not effect the number of dimers at room temperature.

The spectra of the zinc salts given in **Fig. 5.29** show no decrease in the relative absorption intensity of the carboxylate groups compared to the aromatic absorptions although they are partially obscured by coincident absorption bands.

The difference in the rates of degradation between the copolymers and their zinc salts at 350°C is due to a number of different factors. The greater rate of decomposition of the carboxylic acid groups compared to the

styrene units and zinc carboxylate groups, although increasing the number of acid groups in the copolymers appeared to have no significant effect on the rate of degradation in the acid copolymers. The crosslinking in the zinc salts of the copolymers slows down the rate of diffusion of the gaseous decomposition products out of the sample and this may be the rate determining step of the reaction. Slow diffusion of volatile products from the degrading polymer makes possible the intervention of side reactions or back reactions such as polymerisation, thereby complicating the overall process and obscuring the primary reaction and slowing the overall rate of degradation.

From the results comparing the different zinc salts (**Fig. 5.24-26**) it can be seen that the greater the number of crosslinks in the copolymer the slower the rate of degradation. The absence of any difference in the rate of degradation in the copolymer containing 1.7% acrylic acid units is because the small number of acrylic acid units results in fewer crosslinks and less hindrance to the diffusing degradation products. Crosslinking will interfere with the intramolecular transfer reactions occurring in the styrene sequences.

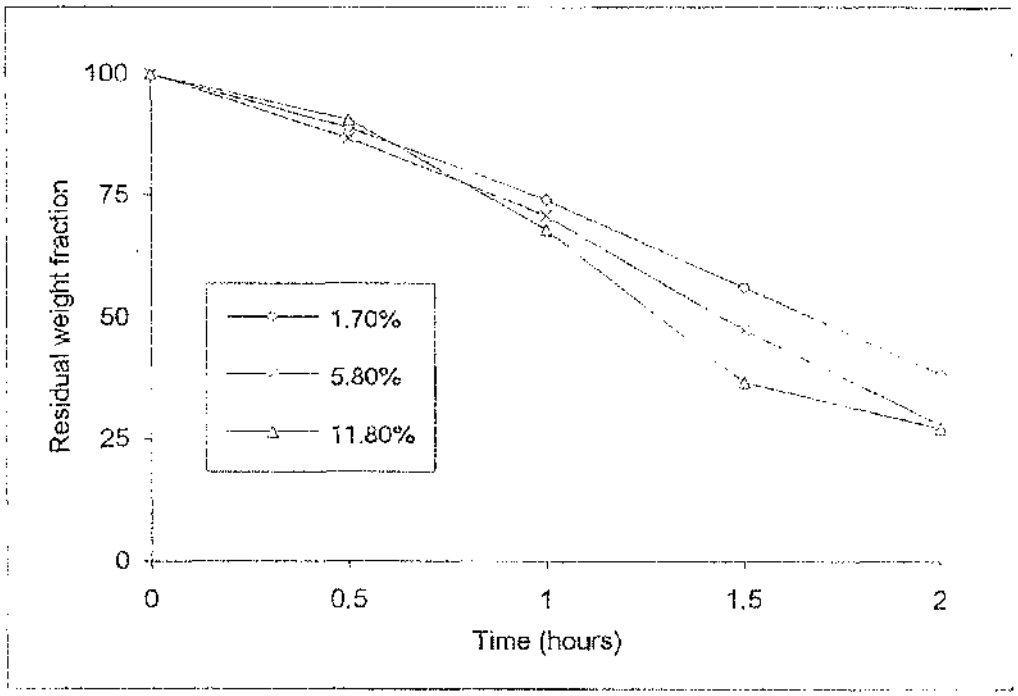


Fig. 5.23 Isothermal heating at 350°C of acid copolymers.

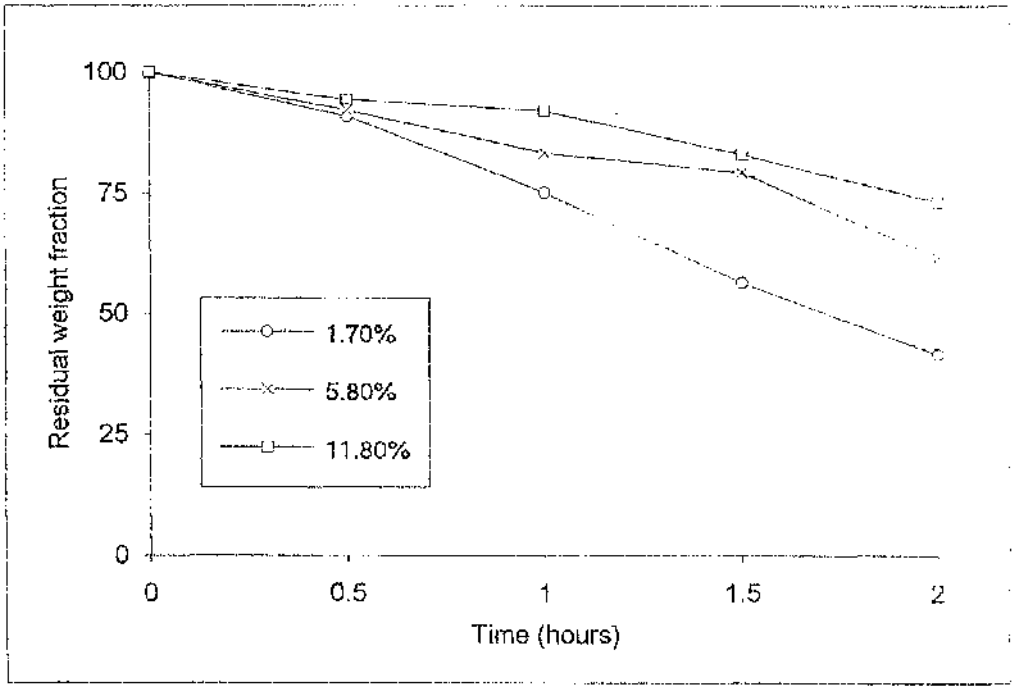


Fig. 5.24 Isothermal heating at 350°C of zinc salts of copolymers.

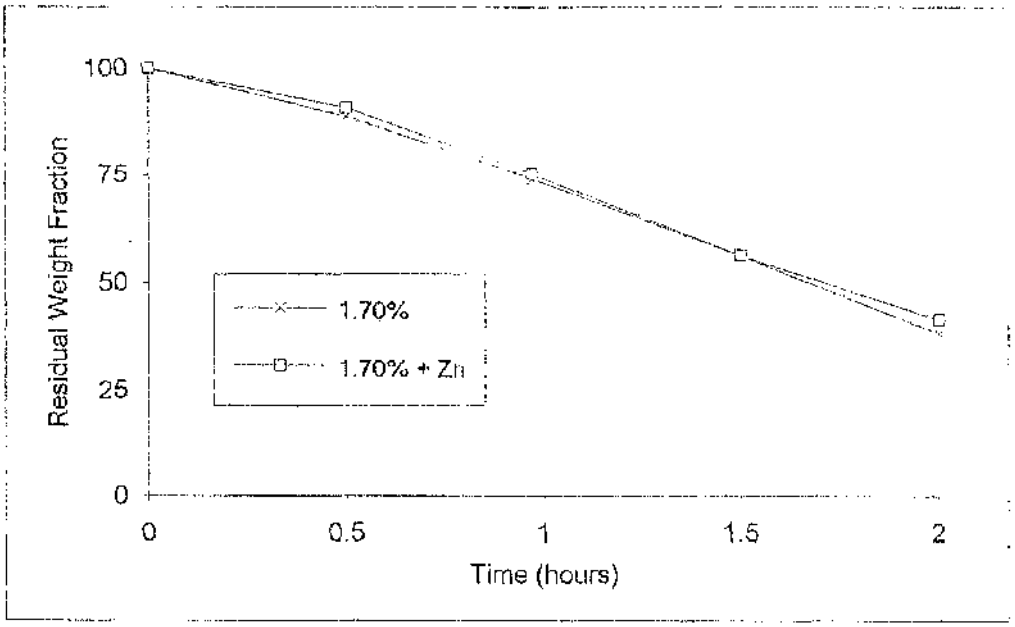


Fig. 5.25 Isothermal heating at 350°C of the styrene/acrylic acid copolymer containing 1.7% acrylic acid units and its zinc salt.

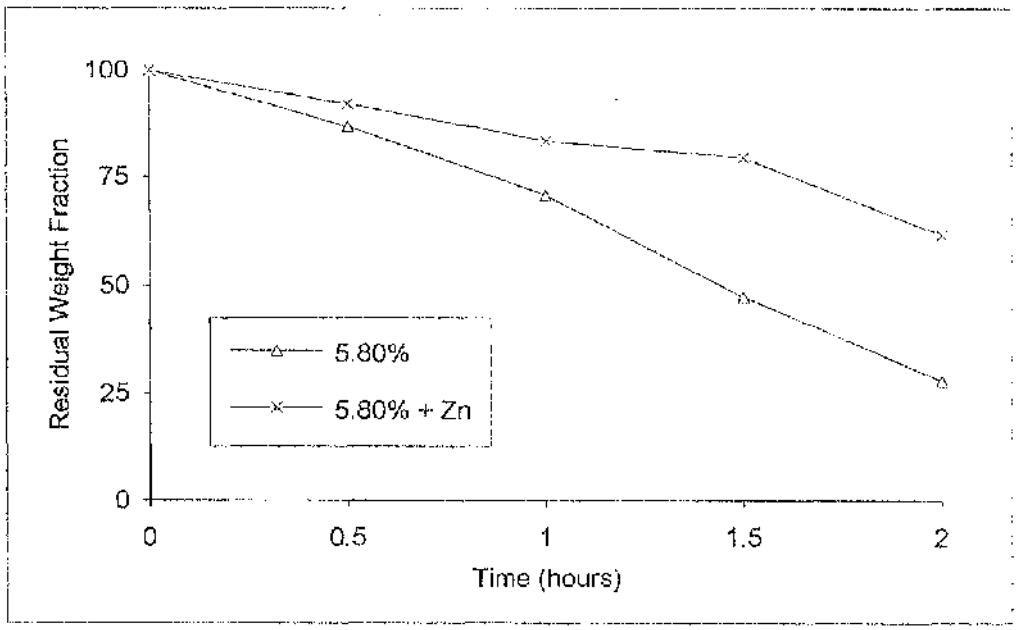


Fig. 5.26 Isothermal heating at 350°C of the styrene/acrylic acid copolymer containing 5.8% acrylic acid units and its zinc salt.

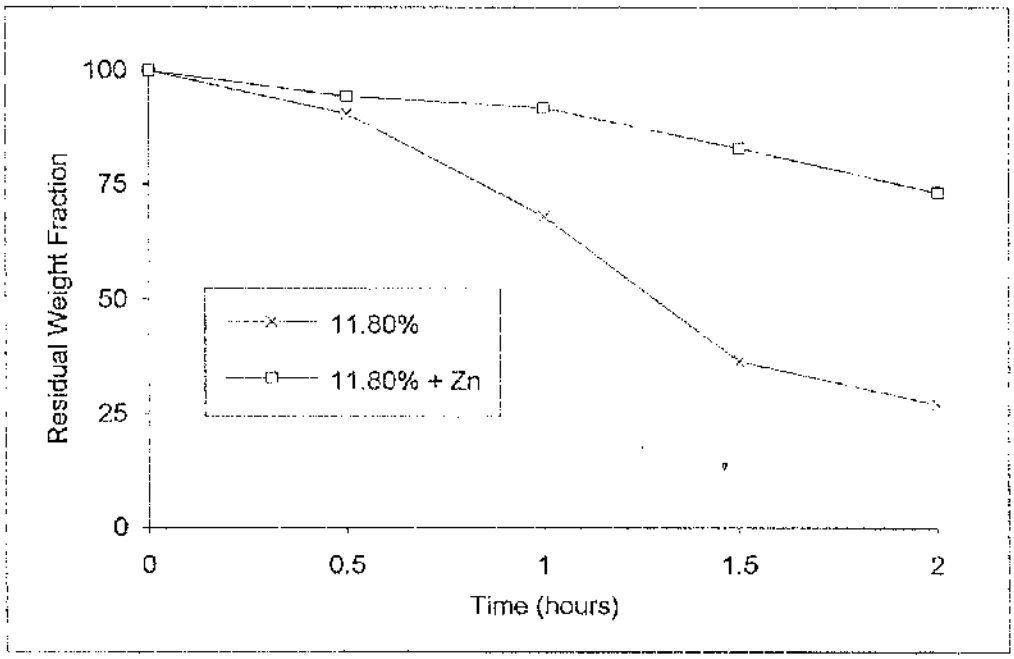


Fig. 5.27 Isothermal heating at 350°C of the styrene/acrylic acid copolymer containing 11.8% acrylic acid units and its zinc salt.

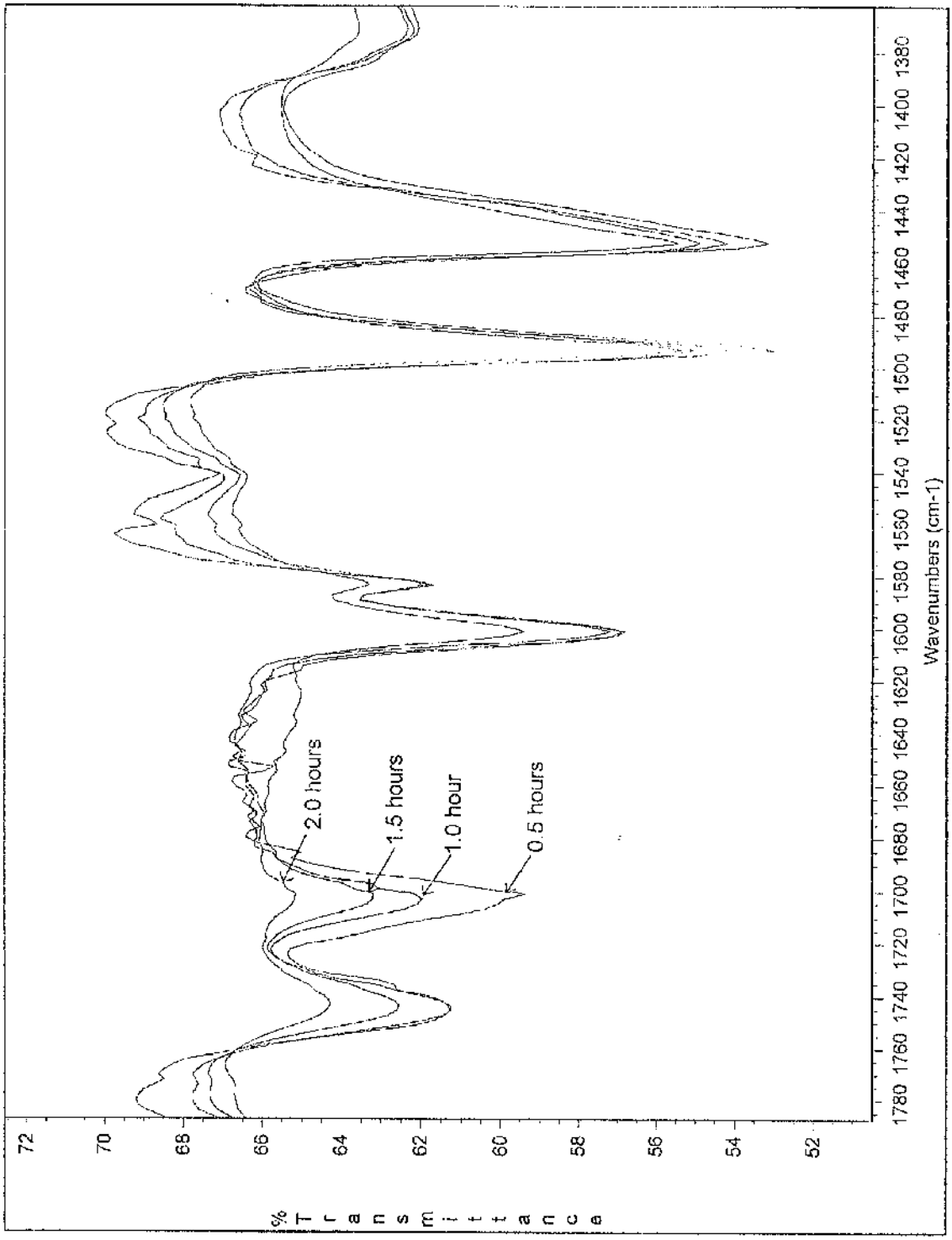


Fig. 5.28 Infra-red spectra of acrylic acid/styrene copolymer, containing 5.8% acrylic acid units, heated at 350°C under vacuum.

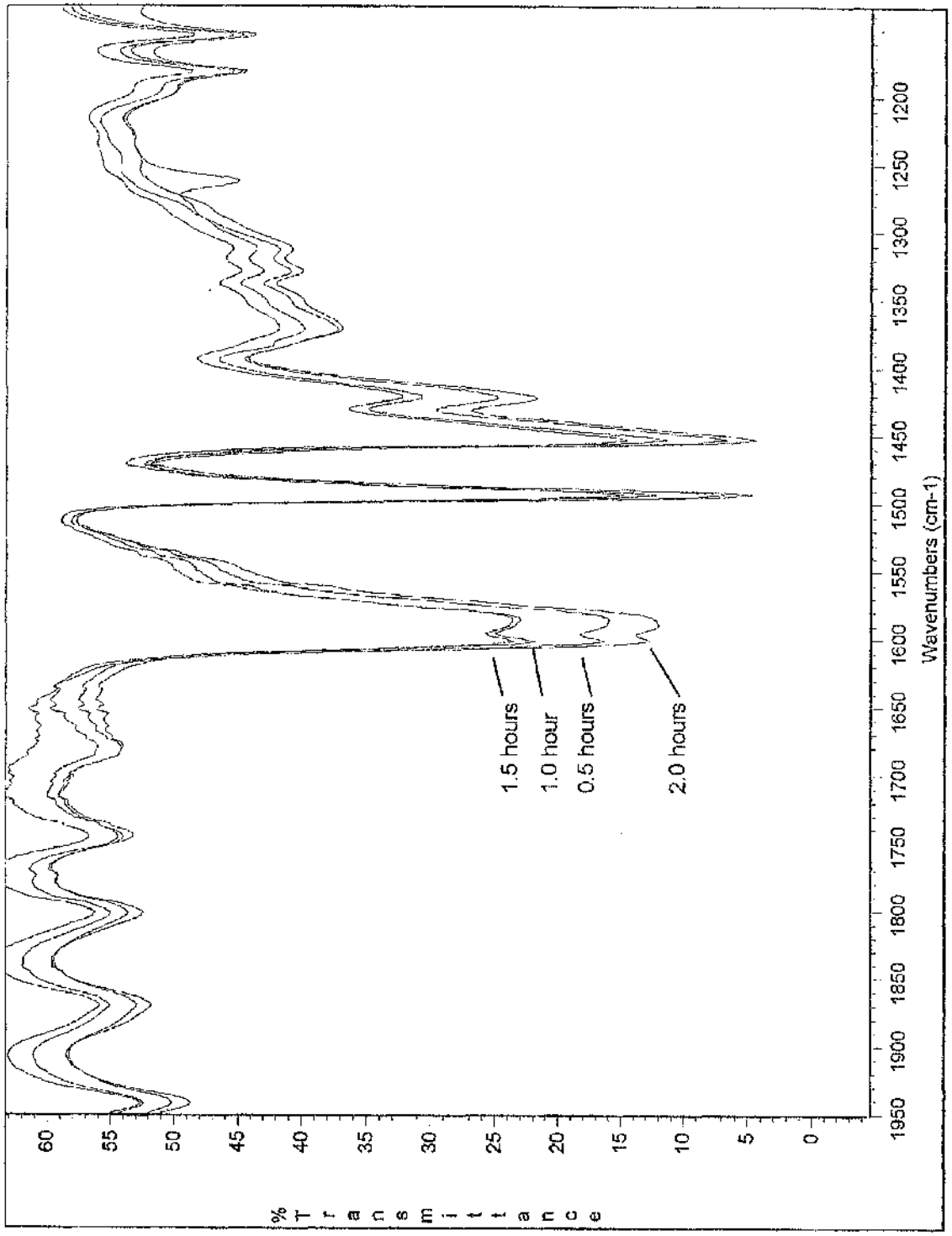


Fig. 5.29 Infra-red spectra of zinc salts of acrylic acid/styrene copolymer, containing 5.8% acrylic acid units, heated at 350°C under vacuum.

5.6 DISCUSSION OF RESULTS

The results obtained from thermogravimetry and DSC indicate that increasing the number of acrylic acid groups results in a small decrease in the thermal stability of the copolymers. Increasing the number of acrylic acid groups from 1.7% to 11.8% resulted in the temperature of maximum rate of weight loss decreasing by 14°C. This trend was not seen in the TVA results where an increase in the number of acrylic acid groups from 1.7% to 11.8% caused the temperature of the rate of maximum evolution of volatiles to increase by 3°C.

It was also seen from thermogravimetry, DSC and TVA that by converting the acrylic acid groups to the zinc acrylate groups an increase in thermal stability was achieved relative to the unneutralised copolymer. No clear trend in thermal stability was seen by increasing the number of ionic groups. Thermogravimetry and DSC appear to show a decrease in thermal stability by increasing the number of zinc acrylate groups while in TVA increasing the number of ionic groups had no effect.

A possible explanation for the discrepancy of the thermogravimetry and TVA results is the method used in detection of volatiles in TVA. The formation of zinc carboxylate groups was found to reduce the amount of styrene oligomers in the cold ring fraction, by inhibiting intramolecular transfer reactions, in favour of monomer formation. Styrene is not condensed by the water condenser and is detected by the Pirani gauges on the vacuum line unlike the cold ring products which do not register on the pirani gauges, whereas both volatilisation of oligomers and monomer is detected by the balance used in thermogravimetry.

The small temperature differences, of less than 10°C, in the results obtained make any small experimental errors in recording sample temperature or the variable measured as a function of sample temperature

significant. It was also clear from the results that using different analysis methods produced different results. Previous works by different authors have stated that both an increase and a decrease in stability were obtained with increasing metal content.[92,93] The differences in the results obtained between TVA and thermogravimetry and DSC may be caused by condensation of the cold ring fraction, amounting to approximately 30-40% of volatile products, before the Pirani gauges used to detect the degradation products in the TVA experiments. The difference in temperature of degradation may also be due to the thermogravimetry and DSC experiments being carried out under nitrogen flow, while the TVA experiments were carried out under vacuum.

The reason for the decrease in thermal stability with increasing acrylic acid content is thought to be because the acrylic acid groups are less stable than the rest of the structure and their decomposition results in the formation of macroradicals from which the unzipping or intramolecular transfer reactions occur leading to the identified degradation products. The isothermal heating experiments show no increase in the rate of weight loss at 350°C by increasing the number of acrylic acid units in the copolymers. From this it can therefore be said that the acrylic acid groups degrade at a higher temperature than 350°C and their contribution to the rate of degradation only becomes important at higher temperatures.

The increase in stability with the addition of zinc ions to the polymer produces a more thermally stable zinc acrylate group than the carboxylic acid group. Comparison of the degradation temperatures of the copolymers with zinc polyacrylate studied in chapter 4 shows the maximum rate of degradation of zinc polyacrylate not occurring until 465°C. This will result in the carboxylic groups being removed as a point of weakness in the polymer chain. As was seen in the isothermal heating experiments the crosslinking effect of the ionic groups will also slow the diffusion of the

gaseous degradation products through the polymer matrix resulting in a slower rate of degradation.

Due to the large mole fraction of styrene in these copolymers the mechanism of degradation will be broadly similar to that of polystyrene. The small number of acrylic acid units in the copolymers and the reactivity ratio of acrylic acid in the copolymerisation with styrene (Chapter 3.10) makes it unlikely for neighbouring acrylic acid groups to occur in the copolymers. Dehydration reactions to form acid anhydride structures and their subsequent decomposition, as is found in the thermal degradation of poly(acrylic acid), are therefore considered to be unlikely.

Polystyrene as described in section 5.1 is believed to degrade thermally by processes which involve unzipping to form styrene and intramolecular transfer reactions resulting in styrene oligomers (**Fig. 5.30**). It has been suggested that the initiation of degradation occurs by two possible routes involving benzyl (A) or vinyl (B) groups near the chain ends leading to macroradicals (C) and (D), with the two smaller corresponding radical species (E) and (F) providing the source of the minor products toluene and α-methylstyrene, respectively.

It is thought that structure (D) is the main source for the competing depropagation and intramolecular transfer reactions that lead to either monomer (G) or oligomers (H). Intermolecular transfer reactions are believed to occur between radical species such as (C), (E) or (F) and the polymer chain which lead to the vinyl end structure (B) and to structure (D) the source of depropagation and intramolecular transfer.

Carboxylic acid groups, believed to be α-β-unsaturated, were found in the cold ring fractions of all the copolymers. Hydrogen abstraction as seen in structure (D) in **Fig. 5.30** where the phenyl group is replaced with a

carboxylic acid group can lead to a structure similar to (H) except an unsaturated chain end containing a carboxylic acid is formed. A radical containing a carboxylic acid group and an α-hydrogen atom group is less stable than one with an aromatic group and this will act as a block to depolymerisation increasing the favourability of transfer reactions which will result in carboxylic acid containing oligomers. A small increase in the amount of cold ring fraction with increasing carboxylic acid content is seen in table 5.2.

A possible mechanism for the formation of benzaldehyde, a minor degradation product, found in the copolymers containing 5.8% and 11.8% acrylic acid units and their zinc salts is shown in **Fig. 5.31**. Side group scission of the acrylic acid or zinc acrylate group results in structure (A). The radical species (A) then undergoes a radical substitution reaction with the neighbouring aromatic ring resulting in structure (B). This radical species is a site for depropagation or transfer reactions. Side group scission and hydrogen atom abstraction of the structure (B) will result in benzaldehyde formation and could also lead to some of the 3 or 4 carbon atom alkyl substituted aromatic compounds found as minor degradation products.

It is also possible that benzaldehyde results from the decomposition of peroxide groups that are incorporated into styrene polymers and copolymers synthesised by free radical processes.

It has been suggested that the two minor degradation products toluene and α-methylstyrene are formed from the initial step in polymer decomposition where the benzyl and vinyl end groups are formed (**Fig. 5.30**). Intermolecular hydrogen atom abstraction reactions between radicals (E) and (F) and the copolymer will lead to toluene and α-methylstyrene.

Hydrogen atom abstraction from structure (I) also results in the creation of vinyl end groups found in (B).

Table 5.3 contains the amounts of styrene, toluene and α-methylstyrene found for each of the copolymers expressed as a percentage of the total amount of liquid products found. Comparison of the results obtained for the copolymers and their corresponding zinc salts show that the relative amounts of toluene and α-methylstyrene increase and the amount of styrene decreases on converting the polymers to their zinc salts. From **Table 5.2** it can be seen that the overall amount of styrene obtained in the case of the zinc salts is greater than for the corresponding acid copolymer.

This suggests that the chain constriction caused by the ionic groups makes the intermolecular transfer reactions between the polymer chains and the small radical species (E) and (F) in **Fig. 5.30** more favourable compared to the intramolecular transfer reactions. The intermolecular transfer reactions result in the vinyl end groups of structure (B) which are believed to be the source of α-methylstyrene. Therefore more intermolecular transfer leads to a greater amount of α-methylstyrene as a product, which was found in these experiments, as shown in **Table 5.3**.

The results obtained for the amount of liquid products compared to the amount of cold ring fraction show that the percentage of liquid products in the zinc salts is greater than for the corresponding copolymer. Whereas the amount of cold ring fraction is greater in the copolymer than its zinc salt. From GC-MS analysis of the liquid products of degradation under TVA conditions it was seen that over 95% of the liquid products consisted of styrene.

The trend in the results for the amount of liquid products, mainly in the form of styrene, compared to cold ring fraction obtained is in agreement with those obtained in the degradation of copolymers of styrene with small amounts of divinylbenzene. In these copolymers it was found that the amount of styrene obtained from degradation was increased by increasing the amount of divinylbenzene and hence the number of crosslinks in the copolymer. This is because the carbon carbon bond crosslinks found in styrene/divinylbenzene have the same effect as the ionic crosslinks in the zinc salts of the styrene/acrylic acid copolymers. The crosslinks cause the polymers to have a more rigid structure which inhibits the intramolecular transfer processes in favour of the unzipping reactions resulting in styrene formation.

The conclusion reached from this study of the thermal stability and degradation of copolymers of styrene with acrylic acid is that a small increase in thermal stability is achieved in the zinc salts of these copolymers due to their crosslinked nature slowing the rate of diffusion of gaseous degradation products from the polymer. Comparison of crosslinked and non-crosslinked copolymer degradation products leads to the conclusion that crosslinking of the copolymers causes the formation of degradation products formed from unzipping or intermolecular transfer reactions to be more favourable than those formed by intramolecular transfer.

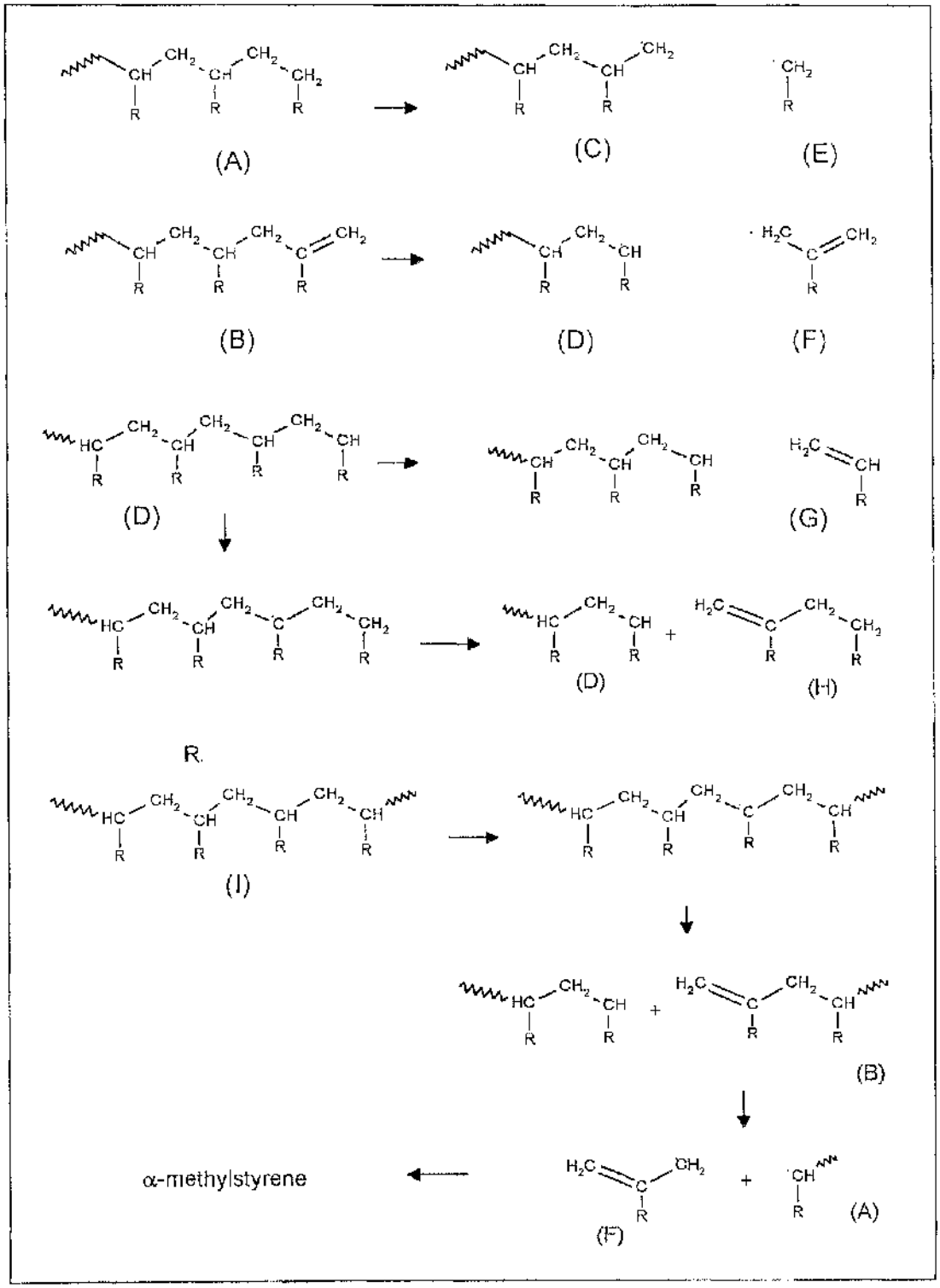


Fig. 5.30 Mechanism of degradation of copolymers.

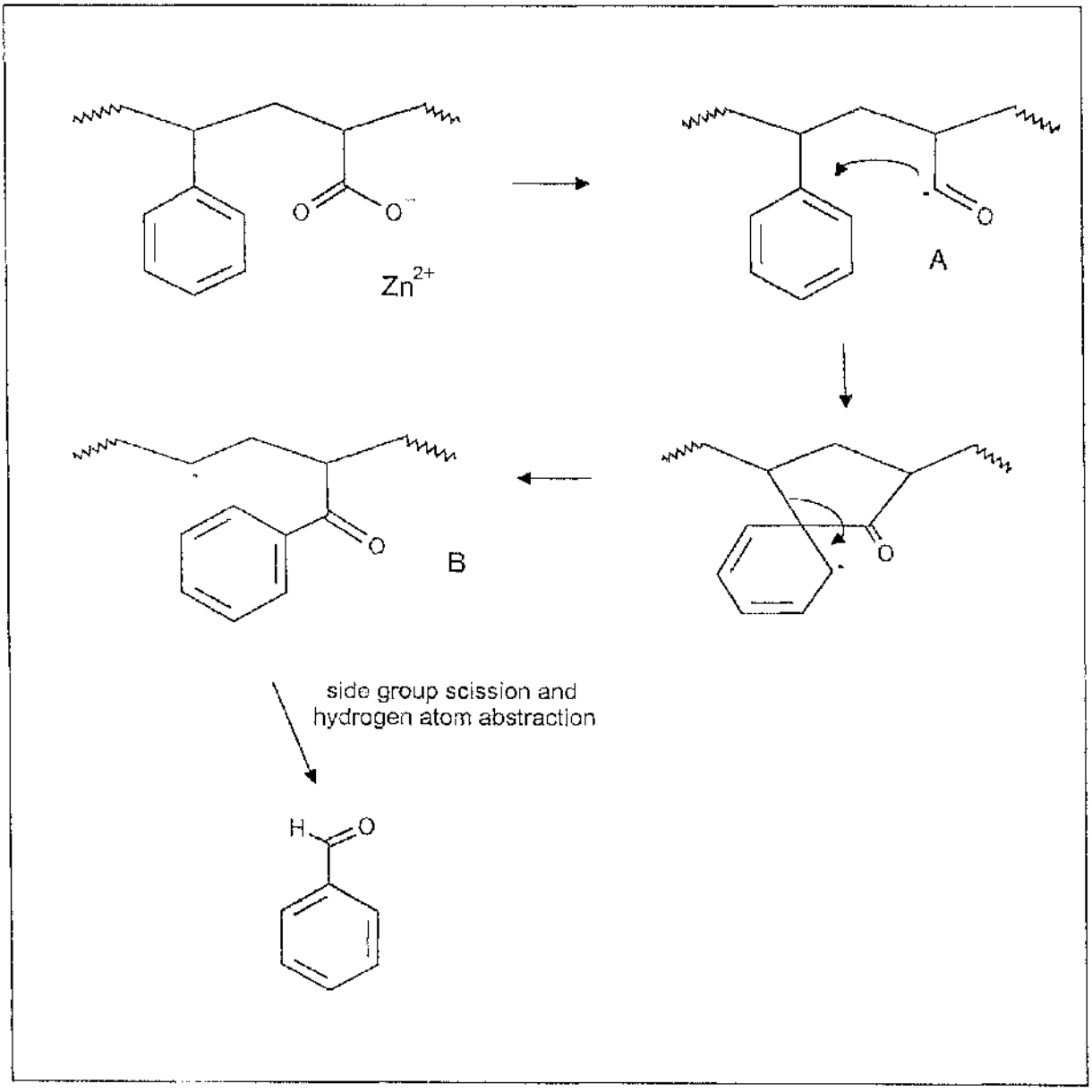


Fig. 5.31 Mechanism of benzaldehyde formation.

REFERENCES

1. Staundinger, H., Ber., **53**, 1073 (1920).
2. Brown, H.P., *Rubber Chem. Tech.*, **30**, 1747
3. Fitzgerald, W.E. and Nielsen, L.E., *Proc. Roy. Soc.*, **A282**, 137(1964)
4. E.I. Du Pont de Nemours & Co., Inc., *US Patent* 3,264,272
5. M^{c}Neill, I.C., *Europ. Polym. J.*, **3**, 409 (1967)
6. M^{c}Neill, I.C., *Europ. Polym. J.*, **6**, 373 (1970)
7. M^{c}Neill, I.C. & Neill, D., *Thermal Analysis*; Schwenker, R.F. & Garn, P.D. (Eds.) Academic Press, London, **1**, 353 (1969)
8. Wojtczak, Z. & Gronowski, A., *Polimery*, **27**, 471 (1982)
9. Fields, J.E. & Nielsen, L.E., *J. Appl. Polym. Sci.*, **12**, 1041 (1968).
10. Smith, D.C. (1969) British Patent 1,139,430.
11. Saviotti, P.P. & Gilson, D.F.R., *J. Phys. Chem.*, **80**, 1057 (1976).
12. Morawetz, H. & Rubin, I.D., *J. Polym. Sci.*, **57**, 669 (1962).
13. Pomogailo, A.D., Savostyanov, V.S. & Ponomarev, V.I., *Kinet Katal*, **30**, 1414 (1989).
14. Bolgiano, N.C. *Brit., UK Pat Appl.*, GB 2,107723.
15. Niki, M. & Ootani K. (Daikar Kogyo Co. Ltd) *Jpn Kokai Tokkyo Koho*, JP 01,196,302.
16. M^{c}Neill, I.C. & Zulfiqar, M., *Polym. Deg. & Stab.*, **30**, 267 (1990).
17. M^{c}Neill, I.C. & Zulfiqar, M., *Polym. Deg. & Stab.*, **1**, 89 (1979).
18. Skupinska, J., Wilczura, H. Boniuk, H. *J. Therm Anal.*, **31**, 1017 (1986).
19. Zuliqar, M., Hussain, H., Zulfiqar, S., Mohammad, D., & McNeill, I.C. *Polym. Deg. & Stab.*, **45**, 115 (1994).
20. Meites, L., *Handbook of Analytical Chemistry*, M^{c}Graw-Hill, N.Y., 1963, 1st Ed.
21. Moore, E.R., *Encylopedia of Polymer Science and Engineering*, Wiley Interscience, N.Y., 1989, Vol. 16.
22. Sakota, K. And Okaya, T., *J. Appl. Polym. Sci..*, **20**, 1745 (1976).

23. Nakamura, Y Okubo, M & Matsumoto, T., *Kobunshi Robunshu*, **39**, 473 (1982).
24. Chapin, E.C., Ham, G.E. & Mills, C.L., *J. Polym. Sci.*, **4**, 597 (1949) *erratum J. Polym. Sci.* **55**, S-6 (1961).
25. Greenley, R.Z. *Polymer Handbook*, John Wiley & Sons, N.Y. 1975, 3rd Ed, 11/165.
26. Bevington, J.C., Ghanem, N.A. & Melville, H.W., *J. Chem. Soc.* 2822 (1955).
27. Nyquist, R.A. Platt, A.E. & Priddy, D.B., *Appl. Spectrosc.*, **36**, 417 (1982).
28. Haken, J.K. & Tan, L., *J.Polym. Sci. Part A, Polym. Chem. Ed.*, **26**, 1315 (1988).
29. Cameron, G.G. & Kane, D.R., *J. Polym. Sci. B*, **2**, 693 (1964).
30. Cameron, G.G. & Kane, D.R., *Makromol. Chem.*, **109**, 194 (1967).
31 Haken, J.K., Ho, D.K.M. & Houghton, E., *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1163 (1974).
32. Grassie, N. & Speakman, J.G., *J. Polym. Sci., A-1*, **9**, 919 (1971).
33. Hodder, A.N., Holland, K.A. & Rae, I.D., J. *Polym. Sci., Polym. Lett. Ed.*, **21**, 403 (1983).
34. M^{c}Neill, I.C. & Sadeqhi, S.M.T., *Polym. Deg. & Stab.*, **30**, 213 (1990).
35. M^{c}Neill, I.C. & Sadeqhi, S.M.T., *ibid.*, **30**, 267 (1990).
36. Hetper,J., Balcerowiak, W. & Beres, J., *J Thermal Anal.*, **20**, 345 (1981).
37. M^{c}Neill, I.C. & Zulfiqar,M., *J. Polym. Sci., Polym. Chem Ed.*, **16**, 3201 (1978).
38. M^{c}Neill, I.C. & Zulfiqar, M., *Polym. Deg. & Stab.*, **1**, 89 (1979).
39. Furukawa, S. & Naruchi, K., *Chiba Diagaku Kogakubu Kenkyu Kokoku,* **16** 83 (1965).
40. Furukawa, S. & Naruchi, K., *Ibid.*, **16**, 92 (1965).
41. Furukawa, S & Kumakaw, N., *Chiba Diagaku Kogakubu Kenkyu Kokoku,* **17,** 33 (1965).
42. Katsube, M., *Jpn Kokai Tokkyo Koho,* JP 61,103,456
43. Sawai, K., *Jpn Kokai Tokkyo Koho,* JP 63,81,116

44. Fukura, Y, Morimura, Y. Ishikawa, H, Tanuma, I & Honda, T., *Jpn Kokai Tokkyo Koho* JP 63,234,044

45. Dzardimaleva, G.I., Pomogailo, A.D., Dubovitski, A.V., Topnikov, V.N., Makova, M.K. & Ponomarev, A.N. Dokl. Akad. Nauk. SSSR, **318**, 378 (1991).

46. Crugnola, A., Pegoraro, M. & Severini, F., *J. Polym. Sci., Part C*, **16**, 4547 (1969).

47. Eisenberg, A., Yokoyama, T. & Sambalido, E., *J. Polym. Sci., Part A-1*, **7**, 1717 (1969).

48. McGaugh, M.C. & Kottle, S., *J. Polym. Sci., Part B*, **5**, 817 (1967).

49. McNeill, I.C. & Sadeghi, S.M.T., *Polym. Deg. & Stab.*, **29**, 233 (1990).

50. Grant, D.H. & Grassie, N., *Polymer*, **1**, 125 (1960).

51. Bamberger, E., *Chem. Ber.*, **43**, 3517 (1910).

52. Miller, A.L., Cook, N.C. & Whitmore, F.C., *J. Am. Chem. Soc.*, **72**, 2732 (1950).

53. Bell, J. & Reed, R.I., *J. Chem. Soc.*, 1383 (1952).

54. Nicholson, J.W. & Wison, A.D., *Br. Polym. J.*, **19**, 67(1987).

55. Nicholson, J.W. & Wison, A.D., ibid., **19**, 449 (1987).

56. Nicholson, J.W., Wassan, E. & Wison, A.D., *Br. Polym. J.*, **20**, 97 (1988).

57. Gronowski, A. & Wojtczak, Z., *J. Thermal Anal.*, **26**, 233 (1983).

58. Dzhardimalieva, G.I; Pomogailo, A.D; Davityan, S.P; Ponomarev, V.I.,*Izv. Akad. Nauk SSSR Ser. Khim.*, **7**, 1531 (1988).

59. M^{c}Neill, I.C., Zulfiqar, M. & Vrie, C., *Polym. Deg. & Stab.*, **9**, 239 (1984).

60. Zulfiqar, M., Hussain, R., Zulfiqar, S., Mohammad, D. & M^{c}Neill, I.C., *Polym. Deg. & Stab.*, **45**, 115 (1994).

61. Nyqist, R.A. & Kagel, R.O., *Infrared Spectra of Inorganic Compounds*, Academic Press, London, 1971.

62. Fields, J.E. & Neilson, L.E., *J. Appl. Polym. Sci.*, **12**, 1041(1968).

63. Wall, F.T. & Drenan *J. Polym. Sci.*, **7**, 83 (1951).

64. Mandel, M. & Leyte, J.C., *J. Polym. Sci. Part A.*, **2**, 2883 (1964).

65. Wall, F.T. & Gill, S.J., J. *Phys. Chem.*, **58**, 1128 (1954).

66. Gregor, H.P., Luttinger, L.B. & Loebel, E.M., *J. Phys. Chem.*, **59**, 366 (1955)
67. Gregor, H.P., Luttinger, L.B. & Loebel, E.M., *Ibid.*, **59**, 35 (1955)
68. Deacon, G.B. & Phillips, R.J., *Aust. J. Chem.*, **31**, 1709 (1978).
69. Irving, H. & Williams R.J.P., *J. Chem. Soc.*, 3192 (1953).
70. Yokobayashi, H., Nagase, K. &Muraishi, K., *Bull. Chem. Soc. Japan*, **48**, 2789 (1975).
71. Edwards, D. A. & Hayward, R.N. *Can. J. Chem.*, **46**, 3443 (1968).
72. Kornienko, W.P., *Ukr. Khim. Zh.*, 23, 159 (1957).
73. Cameron, G.G., Meyer, J., % McWalter, I.T., *Macromolecules*, 11, 696 (1978).
74. Chiantore, O., Camino, G., Costa, L., & Grassie, N., *Polym. Deg. & Stab.*, **3**, 209 (1981).
75. Costa, L., Camino, G., Guyot, A., Bert, M. & Chiotis, A., *ibid.*, **4**, 245 (1982).
76. McNeill, I.C. & Stevenson, W.K.T., *ibid.*, **10**, 247 (1985).
77. Guaito, M. Chiantore, O., & Costa, L., *ibid.*, **12**, 315 (1985).
78. Costa, L., Camino, G., Guyot, A., Bert, M., Clouet, G. & Brossas, J., *Ibid.*, **14**, 85 (1986).
79. Guyot, A., *ibid*, **15**, 219 (1986).
80. Staudinger, H. *Ber.*, **59**, 3019 (1926).
81. Billmeyer, F.J., *Textbook of Polymer Science*, Wiley Interscience, N.Y, 1985 3rd ed. Ch. 14 p 387
82. Eisenberg, A., *Macromolecules*, **3**, 147 (1970).
83. Roch. E.J., Stein, R.S., Russel, T.P. & MacKnight, W.J., *J.Polym. Sci., Polym.Phys. Ed.*, **18**, 1497 (1980).
84. Fujimara, M., Hashimoto, T. & Kawai, H., *Macromolecules*, **15**, 136 (1982).
85. Fournet, G. *Acta Crystallogr.*, **4**, 293(1951).
86. Yarusso, D.J. & Cooper, S.L. *Macromolecules*, **16**, 1871 (1983).
87. Lantman, C.W., MacKnight, W.J. & Lundberg, R.D. *Comp. Polym. Sci.*, Pergamon Press, Oxford, 1989, vol. 2 ch. 25.

88. Vollmert, B. & Schoene, W., *Angew. Makromol. Chem.*, **19**, 157 (1971).
89. ibid. Proc. Amer. Chem. Soc. Symp., 1970 (pub. 1971 145-57).
90. Kapse, G.W. & Aggarwal, L.K. *Paintindia*, **33**, 5 (1983).
91. Suchoka-Galas, K., Koscielecka, A., Wojtczak, Z. & Wojdylo, K. *Polimery*, **27**, 383 (1982).
92. Gronowski, A. & Wojtcak, Z., *J. Therm. Anal.*, **30**, 345 (1985).
93. Wlochowicz, A. & Eder, M., *Angew. Makromol. Chem.*, **156**, 139 (1988).
94. McNeill, I.C. & Liggat, J.J. *Polym. Deg. & Stab.*, **36**, 291 (1992).
95. Allan, J.R., Bonner, J.G., Turvey, K., Gerrard, D.L. & Birnie, *J. Plast. Rubber Compos. Process. Appl.*, **15**, 115 (1991).